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Review of biochar role as additive in anaerobic digestion processes

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1 **Review of biochar role as additive in anaerobic digestion processes**

2 Marco Chiappero[a], Omid Norouzi[b], Mingyu Hu[c], Francesca Demichelis[a], Franco

3 Berruti[d], Francesco Di Maria[b], Ondřej Mašek[c], Silvia Fiore[a] *

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5 [a] DIATI (Department of Engineering for Environment, Land and Infrastructures),

6 Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Torino, Italy

7 [b] LAR Laboratory, Department of Engineering, University of Perugia, Perugia, Italy

8 [c] UK Biochar Research Centre, School of Geoscience, University of Edinburgh,

9 Edinburgh, United Kingdom

10 [d] Institute for Chemicals and Fuels from Alternative Resources (ICFAR), Chemical and

11 Biochemical Engineering Department, Western University, London, Ontario, Canada

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13 **corresponding author:** Prof Silvia Fiore, DIATI, Politecnico di Torino, Corso Duca

14 degli Abruzzi, 24; 10129, Torino, Italy; Email: silvia.fiore@polito.it; Phone: +39

15 0110907613

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17 **Abstract**

18 Anaerobic digestion (AD) could be considered as a mature technology and nowadays it

19 can still play a pivot role because of the urgent need to provide renewable energy sources

20 and efficiently manage the continuously growing amount of organic waste. Biochar (BC)

21 is an extremely versatile material, which could be produced by carbonization of organic

22 materials, including biomass and wastes, consistently with Circular Economy principles,

23 and "tailor-made" for specific applications. The potential BC role as additive in the

24 control of the many well-known critical issues of AD processes has been increasingly

25 explored over the past few years. However, a clear and comprehensive understanding of

26 the connections between BC and AD is still missing. This review paper analyses and

27 discusses significant references (review articles, research papers and international

28 databases and reports), mostly published in the last 10 years. This review is aimed at

29 addressing three key issues related to the better understanding of the BC role in AD

30 processes: 1. Investigation of the influence of BC properties on AD performances and of

31 their ability to counteract its main challenges; 2. Assessment of the optimal BC

32 production chain (i.e. feedstock-pyrolysis-activation) to achieve the desired features; 3.

33 Evaluation of the economic and environmental advantages connected to BC use in AD

34 processes, compared to conventional solutions applied to address AD challenges.

35
36 **Highlights**

37 - Biochar key properties were specific surface, pores and surface functional groups

38 - Lignocellulosic biomass, slow pyrolysis and physical activation made the best biochar

39 - Biochar addition exhibited economic and environmental advantages

40 - Biochar improved methane production (in average 25 %) and digestate quality

41

42 **Keywords:** anaerobic digestion; biochar; bioenergy; biomass; circular economy; waste

43

44 **Abbreviations**

45 AD: anaerobic digestion; BC: biochar; BET: Brunauer–Emmett–Teller; CE: circular

46 economy; CEC: cationic exchange capacity; CIC: controlling internal circulation; CLSM:

47 confocal laser scanning microscopy; COD: chemical oxygen demand; DIET: direct

48 interspecies electron transfer; EAC: electron accepting capacity; EDC: electron donating

49 capacity; EU: European union; FAN: free ammonia nitrogen; FISH: Fluorescence in situ

50 hybridization; FW: food waste; GAC: granular activated carbon; GHG: green-house gas;

51 HRT: hydraulic retention time; IET: interspecies electron transfer; LCA: life cycle

52 analysis; MSW: municipal solid waste; OFMSW: organic fraction of municipal solid

53 waste; OLR: organic loading rate; PAH: polyaromatic hydrocarbons; PCBs:

54 polychlorinated biphenyls; S/I: substrate to inoculum ratio; SMP: specific methane

55 potential; SS: suspended solids; SSA: specific surface area; TAN: total ammonia

56 nitrogen; TPAD: two phased anaerobic digestion; TSS: total suspended solids; UASB:

57 up-flow anaerobic sludge blanket; VFA: volatile fatty acids; WAS: waste activated

58 sludge; WWTP: wastewater treatment plant; WV: working volume; V: volume.

59

60 Contents

81

82 1. Introduction

83 The global energy consumption increased from around 8,800 million tonnes of oil

84 equivalents (Mtoe, including coal, gas, oil, electricity, heat and biomass) in 1990 to

85 14,400 Mtoe in 2018 [1]. In 2016 renewable energy sources met this demand for about

86 14 % of primary energy supply, while fossil fuels accounted for 81% of greenhouse gas

87 (GHG) emissions [2]. The need to decrease fossil fuel dependency and GHG emissions

88 and to generate economic benefits is stimulating initiatives to produce energy as well as

89 high-value chemicals and products from sustainable non-food biomass, residues, co-

90 products and wastes.

91 Anaerobic digestion (AD) is a well-established technology for the treatment of

92 wastewater and organic waste, e.g. the organic fraction of the municipal solid waste

93 (OFMSW), waste activated sludge (WAS), animal manure, etc. Biogas can directly

94 replace fossil fuels in heat and power generation or be upgraded to bio-methane as vehicle

95 fuel or injected in the gas grid [3], while digestate can be employed as soil amendment

96 [4,5]. Other benefits of AD, compared to alternative treatment options applied to organic

97 waste, include control of odor and GHG emissions, removal of pathogens and adaptability

98 to many substrates [6]. AD has been extensively implemented, from small-scale

99 applications, particularly in rural areas and developing countries, to large-scale industrial

100 plants [7]. Despite the rapidly growing number of biogas installations in Europe (from

101 about 6,200 to 18,202 between 2009 and 2018) [8], many challenges regarding AD

102 processes still persist. Different options have been explored to address these challenges:

103 optimization of working parameters and bio-reactor configuration, co-digestion and

104 nutrients control [9]; adoption of pre-treatments to enhance the degradability of various

105 substrates [10,11]; use of inorganic and biological additives to support biomass

106 immobilization, supplement nutrients, mitigate inhibitors and improve process stability

107 [12–14].

108 Among the additives, conductive carbonaceous materials, as granular activated carbon

109 (GAC) and biochar (BC), gained interest because of their ability of enhancing methane

110 production [15,16]. BC may present several advantages over other additives; it can be

111 produced with a wide variety of physico-chemical properties by controlling feedstock,

112 pyrolysis operating conditions and the activation process [17,18], resulting "tailor-made"

113 for specific applications. In recent years, several authors confirmed the possibility of

114 increasing methane production through BC addition (Table 1), suggesting different

115 potential mechanisms: (1) increase of the buffering capacity of the AD system; (2)

116 mitigation of inhibition phenomena or agents; (3) support media for biomass

117 immobilization; (4) promotion of syntrophic metabolisms; (5) enhancement of digestate

118 quality; (6) biogas cleaning and upgrading. The most significant and updated scientific

119 literature investigating the BC role within AD processes can be classified as follows

120 (Table 1):

121 - Studies considering the advantages of coupling AD with thermal processes

122   (gasification, pyrolysis and hydrothermal carbonization) from a general point of view;

123 - Studies exploring the positive influence of BC on AD, based on methane and/or biogas

124   production enhancement and/or improvement of digestate quality;

125 - Studies analysing in detail the BC features that may influence one or more of the

126   above-mentioned mechanisms.

127 Considering the digestate, BC has been reported to enhance its quality in terms of nutrient

128 retention, increase of the carbon-to-nitrogen ratio and reduction of nutrient leaching [19].

129 Consequently, BC doesn't need to be separated from digestate at the end of its utilization

130 in AD.

131

132 Table 1. Overview of literature studies exploring the connections between BC and AD

Studies considering the general advantages of coupling AD with thermal processes	Studies exploring the positive influence of BC on AD, based on a general analysis of methane and/or biogas production enhancement	Studies exploring the positive influence of BC on AD, based on a general analysis of the improvement of digestate quality	Studies analysing in details the biochar features that may influence one or more of the six above-mentioned mechanisms
Pecchi and Baratieri, 2019 [20] Fabbri and Torri, 2016 [21] Hübner and Mumme, 2015 [22] Salman et al., 2017 [23]	Linville et al., 2017 [24] Torri and Fabbri, 2014 [25] Sunyoto et al., 2016 [26] Jang et al., 2018 [27] Sun et al., 2019 [28] Zhao et al., 2015 [29] Inthapanya et al., 2012 [30] Inthapanya and Preston, 2013 [31]	Bruun et al., 2011 [32] Shen et al., 2016 [33] Shen et al., 2017 [34]	Fagbohungbe et al., 2017 [19] Ye et al., 2018 [13] González et al., 2018 [15] Zhang et al., 2018 [16] Codignole Luz et al., 2018 [35] Masebinu et al., 2019 [36] Pelaez-Samaniego et al., 2018 [37] G. Wang et al., 2018b [38] D. Wang et al., 2017 [39] Fagbohungbe et al., 2016 [40] Mumme et al., 2014 [41] Shanmugam et al., 2018 [42] Su et al., 2019 [43] Lü et al., 2016 [44] Cruz Viggi et al., 2017 [45] Li et al., 2018 [46] Martínez et al., 2018 [47] Luo et al., 2015 [48] Wang et al., 2019 [49] C. Wang et al., 2018 [50] Zhao et al., 2016 [51] Yu et al., 1999 [52] Cooney et al., 2016 [53] Dang et al., 2017 [54] Sasaki et al., 2010 [55] Martins et al., 2018 [56] S. Chen et al., 2014 [57] Pan et al., 2019b [58] Qiu et al., 2019 [59]

133

134

135 To the best of our knowledge, despite the growing number of studies investigating the

136 connections between BC and AD, three main issues still need to be explored: a clear

137 comprehension of the above-mentioned six mechanisms; a correlation between BC

138 features and their effects on AD processes; environmental and economic outcomes related

139 to BC use. The present review is therefore aimed at addressing the following issues: 1)

140 investigation of the influence of BC properties on AD performance and of their ability to

141 counteract its main challenges; 2) assessment of the optimal BC production chain (i.e.

142 feedstock-pyrolysis-activation) to achieve the desired features; 3) evaluation of the

143 economic and environmental advantages connected to BC use in AD processes, compared

144 to conventional solutions applied to address AD challenges.

145 **2. Review methodology**

146 The selection of scientific literature was made considering the following criteria:

147 a) *Relevant international databases and information sources*. Bibliometric sources as

148 Web of Science, Science Direct and Scopus were used to retrieve articles, book-chapters

149 and proceedings of indexed conferences. Official international databases (Eurostat,

150 International Energy Agency, European Biogas Association, etc.) were searched for the

151 selection of technical reports and statistics;

152 b) *Chronological order*. The majority of the references in this review are from 2015 to

153 2019 (67 %) and from 2009 to 2014 (26 %), with the balance before 2009 (7 %);

154 c) *Relevant keywords for the topics of interest*. A first survey adopted the following

155 keywords in different combinations: "biochar, anaerobic digestion, methane, pyrolysis,

156 economic assessment, environmental assessment, life cycle analysis, LCA". Based on

157 this preliminary selection, the review questions have been identified. Thereby, additional

158 keywords have been adopted to face specific issues, as: "biochar, buffer capacity,

159 anaerobic digestion, volatile fatty acids", "biochar, ammonia inhibition, ammonia

160 removal, anaerobic digestion", "syntrophic metabolisms, biomass immobilization,

161 biochar, anaerobic digestion, DIET, electron transfer".

162 d) *Selection of the references based on content analysis.* After a first screening

163   considering the abstracts of all identified reference sources, 259 relevant references

164   were analyzed as full content and included in this review. The relevant scientific

165   content was sourced from scientific articles (240 research papers and reviews – 93 %),

166   book chapters and indexed conference proceedings (11 documents – 4 %), and

167   international databases and reports (8 documents – 3 %). Considering only the

168   scientific research papers and the reviews, they were related to (Figure 1): AD (31 %)

169   and pyrolysis (10 %); coupling AD and thermal processes (10 %); BC features (25 %);

170   BC and AD interaction mechanisms (14 %); economic and environmental aspects

171   related to BC use (10 %). The distribution of the relative contributes of the scientific

172   literature to the different topics concerning the investigation of BC role in AD in 2009

173   – 2019 exhibits a clear increasing trend due to a growing interest, particularly in the

174   last five years, for the topics covered by the present work and consequently strengthens

175   the need to address the above mentioned review questions.

176 This review is structured according to the contents outline. At the end of each section, the

177 last paragraph summarizes the main findings and research gaps of the specific topic

178 explored, which are finally condensed in the conclusions.

179

180 Figure 1. Relative contributions of the scientific literature selected for this work

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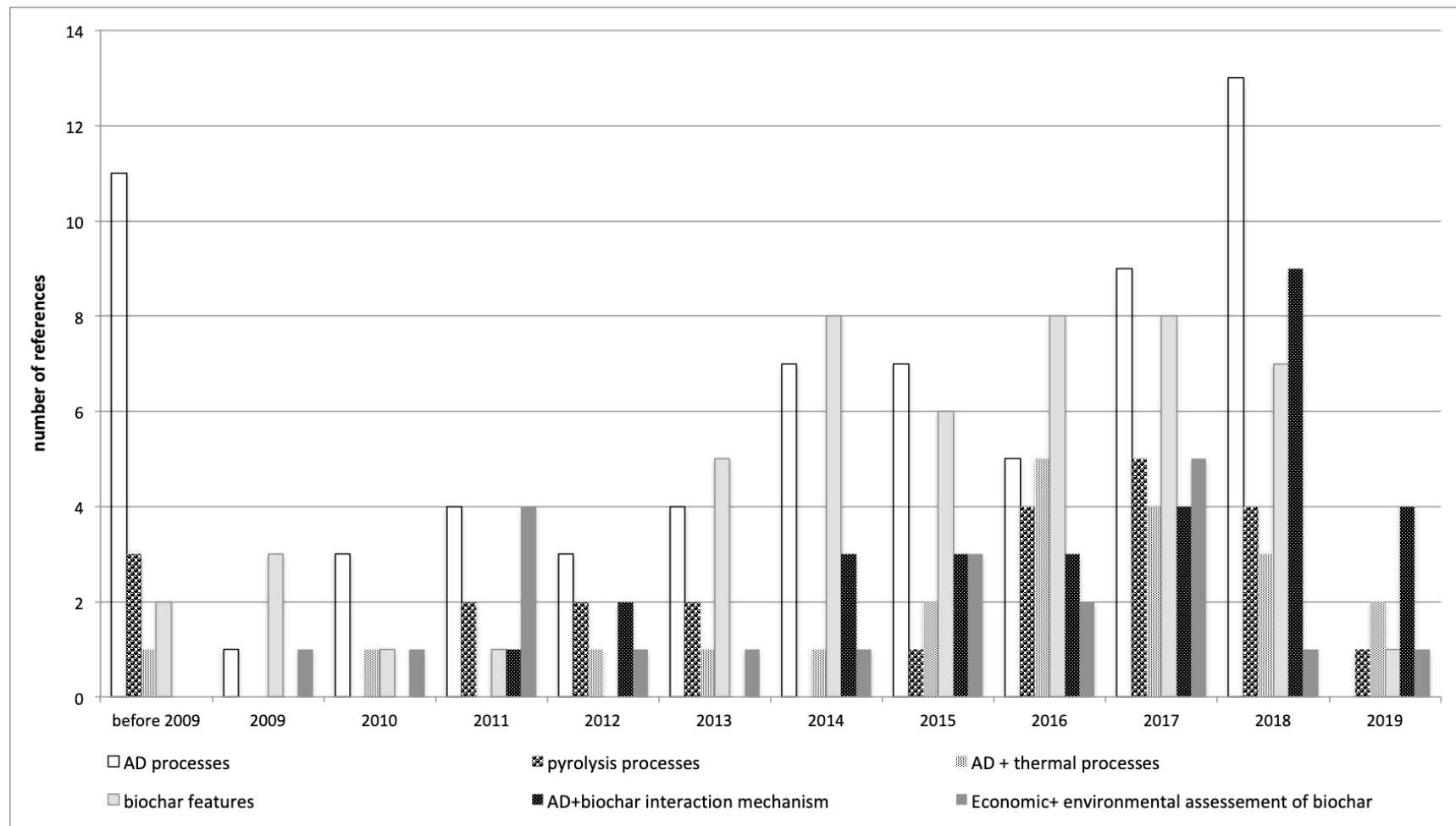
3. Biochar

184 BC is the porous carbonaceous solid residue of the complex physical and chemical
185 phenomena simultaneously occurring during the thermochemical treatment of raw
186 biomass [60–63]. While AD is particularly suitable to produce biogas and digestate from
187 wet organic waste (Figure 2), pyrolysis is a thermochemical process able to convert solid
188 dry biomass in an oxygen-limited environment into valuable liquid chemicals (bio-oil),
189 as well as gaseous biofuels and charcoal (biochar, BC) [64–67]. Although pyrolysis was
190 conventionally mostly focusing on the production of liquid biofuels from woods and
191 purpose-grown energy crops, the most recent studies found that it is not cost effective
192 unless the feedstock is inexpensive, dry and readily available, and there are valuable
193 chemical co-products (liquid bio-oil and solid BC) or favorable government policies [68].
194 Both AD and pyrolysis can contribute to fulfill Circular Economy targets, but research
195 on biological and thermochemical processes traditionally progressed along parallel and
196 separate pathways, often in competition.

197 In recent years, improved understanding of the characteristics of bio-oil and BC has
198 helped to develop key quality requirements to expand their potential value [69]. High
199 value liquid bio-oil products can be obtained from the pyrolysis of biomass residues, such
200 as phenolic substitutes for adhesives or antioxidants [70,71]. However, there are
201 limitations: the most valuable chemicals are usually mixed with impurities that impair
202 their properties. Similarly, there are many promising applications for BC, such as soil
203 improver [18], composite materials [72], activated carbon [73], electrodes for batteries or
204 electrolysis cells [74], metallurgical coke substitute [75], catalyst for tars [76], and could
205 be eligible for carbon credits [77]. The efficiency of BC in most applications significantly

10

206 depends on its physico-chemical properties and elemental composition, which are subject

207 to variations depending on feedstock, pyrolysis conditions, pre- and post-processing

208 treatments.

209 The characteristics of AD and pyrolysis processes and products may offer interesting

210 opportunities for the integration of such technologies (Figure 2), with the objective of

211 contributing to the Circular Economy. For example, pyrolysis could be utilized to convert

212 dewatered digestate into BC, which could then be used for a variety of applications

213 [17,78,79], including its potential use to improve the quality of biogas and digestate [37],

214 or to reduce instabilities and inhibition in digestors [16,24]. On the other hand, the acetic

215 acid-rich aqueous pyrolysis condensate could be utilized as a feedstock for AD, possibly

216 with the addition of BC for the selective adsorption of toxic inhibitors [21–23,25,80–88].

217 In conclusion, BC represents the key link between pyrolysis and AD and, consequently,

218 in this section we wish to review its characteristics, including suitable feedstocks,

219 production technologies, activation processes and characterization techniques.

220

221 Figure 2. Outline of potential integrations between anaerobic digestion and pyrolysis (derived from [20,21]).
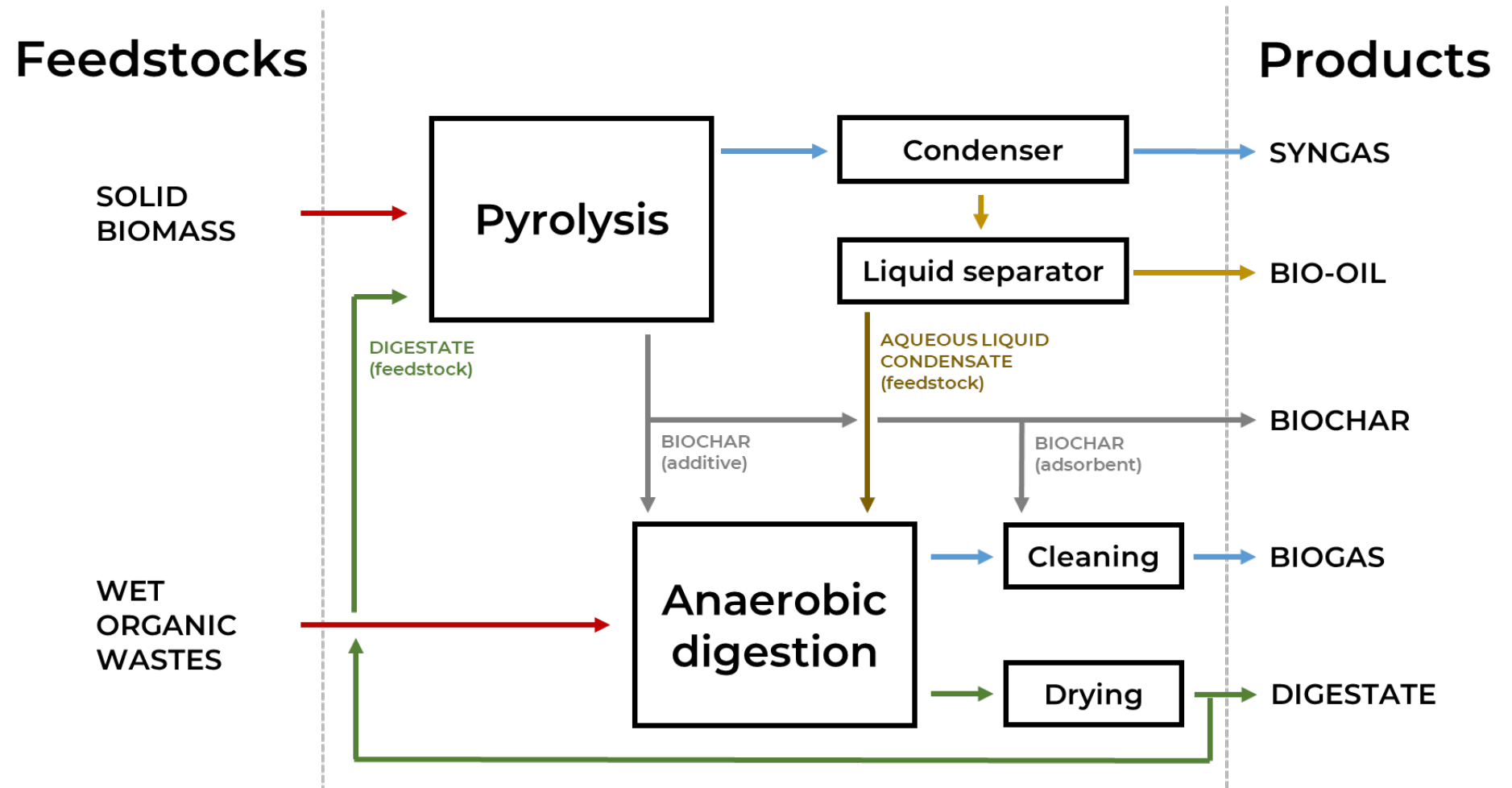
3.1. Feedstocks

225 During thermal processing under oxygen free or oxygen-limited conditions (as pyrolysis),

226 as the temperature increases, the polymeric components of lignocellulosic biomass crack

227 and liquid intermediate phases are formed with different visco-elastic behaviors [89,90];

228 under slow progressive heating, cellulose remains hard and elastic up to 400 °C, whereas

229 hemicellulose softens within a relatively narrow temperature range (230 to 280 °C) and

230 remains viscous, while lignin softens and bubbles over a broader temperature range (150

231 to 350 °C) and remains mainly elastic. The overall process cannot be simply designed

232 based on the linear combination of the behaviors of the individual components, but it is

233 the result of their interactions at different temperatures and it is catalyzed by the mineral

234 matter present in the ashes. As the temperature increases over these ranges, the

235 depolymerized liquid undergoes two competitive processes, oligomer evaporation and

236 crosslinking reactions, with the former favored at high heating rates, and the latter under

237 slow pyrolysis. These findings explain why, under slow pyrolysis, the char yield is

238 greater, and the particles globally keep the same macro-structure of the original biomass,

239 although forming an intermediate soft material. Montoya et al. (2017) [91] confirmed the

240 presence of molten liquid intermediates formed from cellulose, xylan and lignin and

241 showed that the presence of minerals prevents the complete liquefaction of the xylan,

242 therefore contributing to the preservation of the general shape and structure of the solid

243 material during pyrolysis.

244 Therefore, BC can be produced from a wide range of lignocellulosic materials, containing

245 cellulose, hemicellulose (xylan), lignin, small quantities of other organic compounds

246 (phenols, phytosterols and fats) and inorganics (P, N, S, Si, alkali and alkaline earth

247 metals and traces of other minerals). Such materials include wood, agricultural and forest

248 residues, food waste, sugars, industrial organics, sewage sludge and manure. BC can be

249 mesoporous or microporous depending on the operating conditions employed for its

250 production and on the feedstock.

251 *3.2. Thermochemical production*

252 Recent reviews illustrated the different technologies and processes used experimentally

253 and industrially to produce BC [17,92]. These include torrefaction, pyrolysis,

254 gasification, combustion and hydrothermal carbonization [93]. Scale and potential

255 mobility are important considerations in relation to the feedstock supply, logistics,

256 seasonality, further refining, of products quantities, characteristics and value, and

257 potential markets [17,60].

258 *Torrefaction* involves biomass treatment at atmospheric pressure and within a

259 temperature range of 200–300 °C, without oxygen or with limited oxygen supplies [94].

260 As discussed earlier, partial depolymerization and liquefaction of the biomass

261 components take place reducing the biomass tenacity and improving grindability.

262 Torrefaction produces char with less moisture, higher energy density, lower weight, lower

263 O/C and H/C ratio, increased hydrophobic nature and resistance to biological degradation

264 with respect to the original feedstock. Typical yields of torrefied biomass range between

265 50 and 80 % [95].

266 *Gasification* is a thermochemical process carried out at temperatures higher than 750 °C

267 in the presence of a gasifying agent (air, oxygen, or steam) at atmospheric or at high

268 pressures. Under these conditions, biochar yields are not sufficiently significant to

269 consider gasification an appropriate BC production process. Similarly, combustion is not

270 a suitable BC production process, since, under good combustion conditions, BC yield

271 should be negligible.

272 The various modes of *pyrolysis* include slow, intermediate, fast, flash, and ultra-pyrolysis,

273 carried out under vacuum, atmospheric pressure or under pressure [65,69]. As a result of

274 the balance between primary, secondary cracking and recombination reactions, bio-oil

275 yields are typically maximized (up to 70 %) at intermediate temperatures (450-550 °C),

276 faster heating rates (100-500 °C/s) and short vapor residence times (< 1~2 s), which are

277 characteristic of fast and flash pyrolysis. Under these conditions, BC yields are typically

278 of the order of 15~20 %. On the other hand, higher BC yields (25~40 %) are achieved at

279 moderate temperatures (300-450 °C), slower heating rates (~ 1 °C/s) and longer vapor

280 residence times (> 5~10 s), representative of slow or intermediate pyrolysis, when bio-oil

281 yields vary between 40 and 50 % with the balance being gas.

282 *Hydrothermal carbonization (HTC)* is performed on wet biomass (moisture > 10 %) as

283 feedstock, making the process highly energy-intensive [96]. HTC happens under water in

284 a sealed confined system and heated at the temperature range of 175–300 °C for up to 16

285 h under saturated pressure under subcritical conditions producing tar-free BC (hydrochar)

286 with large number of functional groups [97–99]. Hydrochars are usually obtained at

287 yields of 20-25 % [96], and they contain mainly aliphatic compounds and more oxygen

288 functional groups and higher cation exchange capacity than conventional BC. On the

289 other hand, they have lower surface area, microporosity and carbon stability [96,100].

290 Among the various thermal technologies, pyrolysis has been the most investigated

291 technique and it is considered the best technology for the production of BC [101] from

292 relatively dry feedstock (moisture content below 10 %). However, also HTC is gaining

293 interest to produce hydrochar, particularly from wet biomass [96]. In a comparison

294 between the chars, it should be noticed that BC yields are higher, as well as porous

295 structure and aromatics and ash contents, while hydrochar exhibits a non-porous

296 structure, lower fixed and total carbon contents and higher amounts of alkyl functional

297 groups [96].

298 *3.3. Activation*

299 BC with different properties can be produced from a wide range of feedstock and by

300 adjusting processing conditions. Further modification of BC chemical and physical

301 properties can be achieved through a process defined "activation", aimed at increasing

302 BC porosity and modifying its pore size distribution (Figure 3), as well as to some extent

303 surface chemistry. Activation can be carried out in a number of ways, depending on type

304 of activation agents (e.g. physical and chemical activation) or mode of operation into

305 single-stage or multi-stage activation.

306 *Chemical activation* utilizes chemical agents, e.g., H_3PO_4, HNO_3, KOH, NaOH, H_2SO_4,

307 and $ZnCl_2$ [102,103]. It typically involves two steps; in the first the feedstock is

308 impregnated with a selected chemical agent, and then thermally treated in the second step.

309 Another option is the activation of already produced BC by soaking it in a chemical agent,

310 followed by a thermal treatment. Depending on the agent selected and thermal treatment

311 conditions used, different degrees of activation can be achieved. The activated BC needs

312 to be thoroughly washed with deionized water to neutralize its pH and to remove any

313 remaining chemicals [104], and this procedure can contribute to a negative environmental

314 impact of the technology. Oxidative activation that uses acidic or alkaline agents is among

315 the most common activation methods. Besides enhancing porosity and surface area, it

316 also creates oxygen-containing functional groups on the surface of BC (e.g. carboxyl,

317 hydroxyl, lactone, phenol, carbonyl, and peroxide groups). These functional groups play

318 an essential role in different applications of BC, such as for contaminant removal or

319 nutrient sorption.

320 *Physical activation* does not utilize chemicals, thus avoiding some of the negative

321 environmental impacts that can be associated with chemical activation. Instead, BC is

322 exposed to physical oxidizing agents, such as steam, CO_2, ozone or air/O_2, typically at

323 temperatures above 700 °C. These gaseous agents penetrate the internal structure of BC

324 gasifying the carbon atoms, which results in opening and widening of pores [105].

325 Similarly to chemical activation, physical activation not only enhances BC porosity, but

326 also modifies its surface functional groups, increasing the abundance of oxygen

327 functional groups [105].

328 In conclusion, both chemical and physical agents can be used effectively to activate BC

329 and obtain high porosity, surface areas over 1000 m^2/g, and modified surface functional

330 groups, tuned to specific applications. The key challenges of BC activation are without

331 any doubt related to their potential negative environmental impacts, mainly for chemical

332 activations, and high-energy intensity need.

333 *3.4. Physico-chemical characteristics*

334 The variability of BC physico-chemical properties resulting from the proper selection of

335 feedstock, pyrolysis and activation can be adapted to a wide range of applications.

336 S*pecific surface area* (SSA), expressed as m^2g^{-1}, is the ratio between the total surface area

337 and the total particle mass of BC [106], commonly determined by Brunauer–Emmett–

338 Teller (BET) analysis. The reported SSA values of BC can vary significantly, in the range

339 10^0 - 10^2 m^2g^{-1} [107,108] depending on pyrolysis temperature and feedstock, and up to

340 over 10^3 m^2g^{-1} after activation. SSA is a key parameter enhancing the adsorption capacity

341 of BC, even if the chemical composition of its surface is determinant in the interactions

342 with other species [109]. SSA is related to BC pore size distribution [18].

343 P*orosity* can be described by the pore volume ($m^3 g^{-1}$) and by the pore size distribution,

344 including micro-, meso-, and macro-pores (respectively < 2nm, 2-50 nm, >50 nm) [110],

345 based on their internal diameters. The relative abundance of these pores produces

346 different BC structures (Figure 3), since micro-pores have the major contribute to BC

347 surface area, micro- and meso-pores are essential for its adsorption capacity, while macro-

348 pores can provide an appropriate habitat for microorganisms [18,111]. Yin et al. (2017)

349 [112] stated that within a proper range, a high temperature results in a large surface area

350 and pore formations. Trigo et al. (2016) [113] found that SSA increased between 350°C

351 and 700 °C for different hardwood biochars, while Chen et al. (2014) [114] revealed an

352 enhanced porous structure of BC from sewer sludge varying the temperature from 500 °C

353 to 900 °C.

354 Specifically considering the effect of the feedstock on BC characteristics [101], yields

355 and aromatic functional groups are much higher from lignin (48.8 %) than from

356 hemicellulose (21.1 %), while no differences were found in the elemental composition of

357 resulting BCs. High lignin and mineral content in the feedstock result in higher yields of

358 BC [115,116]. Woody and grassy biomasses generate a more carbon-rich BC when

359 compared to sewage sludge and manure [32,117,118]. Specifically considering the effect

360 of pyrolysis process on BC characteristics [119], increasing pyrolysis temperature

361 decreased concentrations of aliphatic carbons, oxygenated functional groups, nitrogen,

362 oxygen and hydrogen. However, carbon mass fraction, micropore volume, ash content,

363 fixed carbon and carbon stability increase with higher pyrolysis temperatures.

364

365 Figure 3. SEM micrographs of (A) raw biomass (eucalyptus) and of derived (B) biochar and (C) physically activated biochar (Courtesy of

366 the authors. The samples were produced at ICFAR and analysed at Politecnico di Torino).

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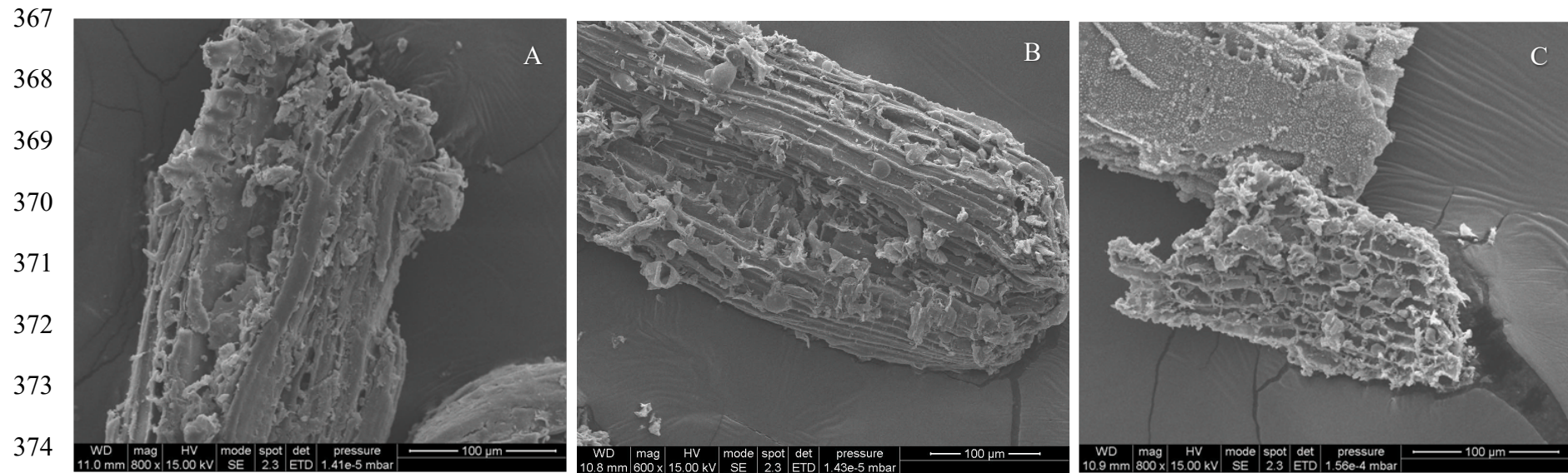
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377 BC *composition* is mainly of C, H, O, N, and S, along with mineral trace components,

378 such as K, Ca and Mg, varying according to pyrolysis conditions and feedstock [110].

379 The mineral content can be enhanced by increasing the temperature of pyrolysis [107].

380 The *cationic exchange capacity* (CEC) of BC can be defined as its ability of absorbing

381 and attracting cations (nutrients and heavy metals) decreasing with higher pyrolysis

382 temperature [18]. A high CEC value is due to a negative surface charge of BC. The

383 presence of *surface functional groups* such as hydroxyl, carboxylic, and amino, expressed

384 respectively as atomic ratio of H/C, O/C, and N/C (generally studied by Fourier transform

385 infrared (FTIR) spectroscopy), mostly depends on the feedstock and it is reduced with a

386 higher temperature of pyrolysis [107]. Further, the H/C ratio is considered as a measure

387 of the degree of aromatization of BC and the O/C ratio as an indication of more

388 oxygenated functional groups, contributing to high CEC values and hydrophilicity of BC

389 [120,121]. An increase in pyrolysis temperature has been reported to negatively affect the

390 amount of acidic functional groups and the CEC [112,122].

391 *pH values* are generally basic and increase as the pyrolysis temperature grows, due to the

392 volatilization of acidic functional groups and to the higher ash content [18]. Moreover,

393 BC can present redox characteristics, being able to donate and accept electrons, and these

394 tendencies are quantified respectively by the *electron donating* and *accepting capacities*

395 [110]. Phenolic groups may be the electron donating species, while quinones and

396 polycondensed aromatic structures the electron accepting compounds [110,123]. In

397 addition, the *electrical conductivity*, expressed as S m^{-1}, decrease as consequence of the

398 increase of the pyrolysis temperature [17].

399 A full characterization of BC involves several analytical methods [124]. Scanning

400 electron microscopy (SEM) is employed to investigate the superficial structure of BC, as

401 well as its chemical composition if coupled with energy dispersive X-ray spectroscopy

402 (SEM-EDX); transmission electron microscopy (TEM) allows to observe BC bulk

403 structure; X-ray diffraction (XRD) analysis detects the crystalline phases; nuclear

404 magnetic resonance (NMR) spectroscopy investigates BC composition, specifically the

405 aromatic structure; X-ray photoelectron spectroscopy (XPS) quantitatively analyses the

406 superficial composition.

407 **4. Application of biochar as additive in anaerobic digestion**

408 *4.1.   Buffer capacity and alkalinity*

409 The volatile fatty acids (VFAs) produced as intermediates during AD tend to lower the

410 pH [125]. This effect is generally counteracted by syntrophic acetogens and methanogens

411 microorganisms, which convert VFAs to methane and carbon dioxide [126]. However, in

412 case of high organic loads of easily biodegradable wastes (i.e. when the VFAs production

413 rate exceeds the consumption rate), the accumulation of VFAs can occur, resulting in pH

414 drop and even in the failure of AD [126,127]. The buffer capacity in a digestor is linked

415 to the ability to neutralize VFAs, and it is considered a rate-limiting step in AD processes

416 [38,39,128]. The buffer capacity is determined by the alkalinity of the AD system, mainly

417 in the form of carbon dioxide and bicarbonate [6,125]. So it is technologically challenging

418 to build a bioreactor aimed at digesting easily biodegradable feedstock with high pH

419 buffer capacity [16]. Even if several methods have been proposed (Table 2) so far, the

420 most diffused solution to improve buffer capacity implemented both at lab [129] and full

421 scale [130] is co-digestion. In particular, manure or sewage sludge showed high buffer

422 capacity, mainly due to the quite high ammonia content, which is able to counteract the

423 pH drop due to VFAs production. Therefore, manure or sewage sludge are often co-
424 digested with OFMSW and/or agricultural waste biomass.

425

426 Table 2. Advantages and disadvantages of conventional methods for creating buffering
427 capacity in bioreactors

Methods	Advantages	Disadvantages
Alkaline pretreatment [131]	Cellulose more available to the enzymes	Expensive and considered as the technological bottleneck
Commercial alkaline materials (e.g. NaOH and $CaCO_3$) [132,133]	Easy pH adjustment	pH continually should be analyzed Temporary Lower biogas output at higher organic loads
Co-digestion [16]	Increasing methane yield Low cost and green	Hard to achieve an appropriate mixture of feedstocks to limit VFAs production
Geopolymer (Composite and monolith) [132,133]	Controllable alkali leaching Prevent the need for continuous pH adjustment	25 g L^{-1} costs around 0.10 $

428

429 However, it still remains a great challenge to develop simple, permanent and cost-
430 effective methods to improve buffer capacity of AD systems. Nowadays, BC is
431 considered as an attractive alternative to the aforementioned methods for two important
432 reasons. Firstly, it can be produced via cost-effective and environmentally friendly
433 approaches. Secondly, its physical and chemical properties can be matched with the
434 operational conditions [19,40,41].

435 BC's buffer capacity mainly depends on two factors:

436 I. *Functional groups*: Rapid accumulation of VFAs during AD process results in a

437   medium with low pH value in which some functional groups of BC like amine

438   adsorbs H^+ and accepts electron. This phenomenon could mitigate the sudden pH

439   drop.

440 II. *Inorganic materials*: Ash portion of biochar contains inorganic materials such as Ca,

441   K, Mg, Na, Al, Fe, Si and S. Among them, alkali and alkaline earth metals (AAEMs)

442   are responsible for alkalinity of biochar via reaction 1 (Ca and CxHxCOOH are

443   selected as representative of AAEMs and VFAs, respectively) [16]:

444        $CaCO_3 + 2C_xH_xCOOH \rightarrow [C_xH_xCOO]2Ca + H_2O + CO_2$ (1)
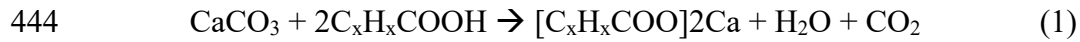
445 Table 3 shows the literature data related to BC buffering capacity and its effects on bio-

446 methane production, showing total alkalinity, pH values and the increase in CH_4

447 production (%), ranging from 8 % up to about 26 %. Some studies suggest that the

448 alkalinity of BC due to AAEMs in ash fraction could effectively contribute to the

449 buffering capacity of AD against VFAs inhibition. Jang et al. (2018) [27] investigated the

450 effects of BC from dairy manure on AD of dry dairy manure at 20°C, 35°C, and 55°C. In

451 each case they observed a lower total VFAs concentration and increased methane

452 production. They suggested the role of high nutrients (9.1% Ca, 3.6% Mg, 1.3% N, 0.14%

453 P) and alkalinity potential of BC in enhancing methane production. Wang et al. (2017)

454 [39] investigated the role of BC from vermicompost on the buffering capacity of AD of

455 high organic loads of kitchen waste and chicken manure. The authors proved the high

456 buffer capacity of vermicompost BC to different short-chain VFAs (700-3800 mg L^{-1}),

457 probably due to the presence of AAEMs and superficial functional groups. Linville et al.

458 (2017) [24] studied the effects of BC from walnut shell during the AD of FW in

459 mesophilic and thermophilic conditions. They observed that BC improved process

460 stability by enhancing the total alkalinity from 2800 to 4800-6800 mg L^{-1} $CaCO_3$ and pH

461 (initial pH >8) in BC amended digesters. Wei et al. (2020) [134] found enhanced methane

462 production and solids removal by adding BC from corn stover (rich of alkaline earth

463 metals) to AD of primary sludge. The authors observed higher total alkalinity (3500-4700

464 mg L^{-1} $CaCO_3$) and pH in BC amended reactors, suggesting that BC provided a strong

465 buffering capacity. Ambaye et al. (2020) [135] investigated the role of BC from sewage

466 sludge on the AD of fruit waste. They observed that the BC addition enhanced methane

467 production and VFAs degradation. Further, the deficiency of some nutrients or trace

468 elements in the substrate may cause an increase of VFAs inducing inhibition of microbial

469 activity during AD [33,135]. Extra doses of trace metals may be required for an effective

470 activity of methanogens without VFAs accumulation [136]. Thereby, it could be

471 speculated that BC could provide adequate concentrations of trace metals for the stability

472 of the AD system [135].

473 In summary, BC addition can counteract VFAs inhibition in case of high loads of easy

474 degradable wastes such as FW, OFMSW, primary sludge. The alkaline nature of BC

475 determining its pH buffering capacity may contribute to prevent VFAs inhibition. The

476 ash fraction of BC contains AAEMs possibly contributing to its acid-buffering capacity

477 and important trace elements for microorganisms. However, further investigations are

478 required to confirm the effectiveness of these mechanisms and to identify the optimal

479 dose of BC related to these properties. Higher doses can be toxic for AD [24,134], perhaps

480 due to inhibitory concentrations of alkali metals [137]. Besides, other mechanisms could

481 be responsible of BC role in alleviating VFAs inhibition. Porous BC could provide

482 support for biofilm growth and protection to selectively enriched functional microbes

483 closely attached to it under acid stress [48]. Secondly, BC could promote the activity of

484 microbial partners enhancing the syntrophic VFAs degradation and methane production

485 under high organic loads [38,138]. The latter microbial mechanisms will be fully adressed

486 in section 4.3.

487

488 Table 3. Results of pH drop and CH_4 production/yield of AD processes in the presence
489 of various types of BCs

Pyrolysis Operational condition				AD Operational conditions				Results of buffering effect					Ref
Temp (C°)	Time (min)	Reactor	Feedstock	Temp (C°)	HRTor duration (d)	Substrate	inoculum	Total alkalinity (g L^{-1} CaCO$_3$)		pH		Increase in CH$_4$ (%)	
								Control	BC	Control	BC		
350	180	Muffle furnace	dairy manure	20	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.18	7.71	26.47[a]	[27]
350	180	Muffle furnace	dairy manure	35	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.09	7.68	24.90[a]	[27]
350	180	Muffle furnace	dairy manure	55	35	dairy manure	Anaerobic sludge	1.8-4.8	5.3-7.3	7.12	7.55	24.69[a]	[27]
500	120	Tube furnace	vermi-compost	35	50	chicken manure	Anaerobic sludge	6.0	7.3	7.0-7.1	7.8-8.0	N.P.	[39]
500	120	Tube furnace	vermi-compost	35	50	kitchen waste	Anaerobic sludge	0.0	2.3	3.5-3.7	4.7-4.9	N.P.	[39]
600	120	Kiln	corn stover	55	15	primary sludge	Anaerobic sludge	2.8	3.5-4.7	7.2	7.6-8.0	8.6-17.8[a]	[134]
350	15		sewage sludge digestate	37		fruit waste	Anerobic sludge	N.P.	N.P.	4.5-5	7-8	13-27[a]	[135]
550	15		sewage sludge digestate	37		fruit waste	Anerobic sludge	N.P.	N.P.	4.5-5.5	7-8.6	12-22[a]	[135]
500	120	Slow pyrolysis	rice straw	35	25	Municipal solid waste	Anaerobic sludge			7.8	7.5	11.69[a]	[139]

a) **CH$_4$ Yield; N.P: Not provided**.

490
491
492 *4.2. Adsorption of inhibitors*

493 Inhibition is often defined as the predominant cause of reduction of bio-methane yields

494 and instability of AD processes. A substance can be identified as "inhibitor" when it

495 determines an adverse shift in the microbial population or arrests of the bacterial growth

496 [137]. There are direct inhibitors, such as metals (Cu^{2+}, Zn^{2+}, Cr^{3+}, Cd, Ni, Pb^{4+}, Hg^{2+},

497 Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}), organic compounds (chlorophenols, halogenated aliphatics,

498 pesticides, antibiotics, lignocellulose hydrolysate); and indirect inhibitors, such as VFAs,

499 long-chain fatty acids, hydrogen, ammonium and sulphides [19]. Among the inhibitors,

500 ammonia (NH_3 or free ammonia nitrogen, FAN) and ammonium (NH_4^+) concentrations

501 are considered crucial (ammonia and ammonium are together considered as total

502 ammonia nitrogen, TAN). The optimal control of ammonia and ammonium may ensure

503 stable bacterial growth and significantly contribute to the buffer capacity of the AD

504 system. However, excess FAN/TAN concentrations are major causes of AD failure

505 [140,141]. Chen et al. (2008) [137] reported a wide range of TAN concentrations

506 (between 1.7 and 14 g L^{-1}) causing a 50 % reduction in methane production. FAN

507 concentration is considered the main cause of inhibitions for methanogens [140,142] and

508 it was reported to have a toxic effect to anaerobes ranging from 150 to 1200 mg L^{-1}

509 [143,144]. Various mitigation strategies have been investigated to effectively counteract

510 TAN/FAN inhibitory effects on AD. Some were based on the removal and

511 immobilization of the inhibitor, as: dilution, co-digestion and microbial adaptation [145–

512 147]; struvite precipitation [148]; use of a microbial desalinisation cell [149]; ammonia

513 stripping [150]. An alternative approach is based on the use of adsorbents, inorganic as

514 zeolites [142] and organic as GAC [143] and BC [41].

515 Based on several studies focusing on BC impacts on AD and ammonia inhibition (Table

516 4), it seems that BC could effectively mitigate ammonia inhibition, resulting in reduced

517 lag phase and enhanced methane production respect to control reactors. Some authors

518 [33,34,151] promoted BC use in AD of sewer sludge. Mumme et al. (2014) [41] revealed

519 that BC from pyrolysis of paper sludge and wheat husks could limit mild ammonia

520 inhibition (2.1 g TAN kg-1). Su et al. (2019) [43] stated that the addition of BC may

521 alleviate inhibition in case of up to 1500 mg L^{-1} ammonia-N in food waste AD [152]. Lü

522 et al. (2016) [44] revealed that BC can support AD under high ammonium stress (up to 7

523 g-N L^{-1}). The above-mentioned studies suggest a positive effect of BC towards ammonia

524 inhibition, however, there isn't full agreement on the mitigation mechanisms

525 hypothesized: cation exchange capacity [34,151]; chemical and/or physical adsorption

526 capacity and surface functional groups [33,34,151]; promotion of direct interspecies

527 electron transfer (DIET) [44,153]; immobilization of microorganisms [43,44].

528 Therefore, BC may contribute to ammonia mitigation by direct (cation exchange capacity,

529 adsorption, surface functionality) and/or indirect factors (DIET and immobilization of

530 microorganisms), depending on the characteristics of both BC and digested substrate,

531 along with the operating conditions of the AD process (e.g. pH and temperature).

532 Focusing on direct factors, a better understanding of the interactions between BC and

533 FAN/TAN is a key step to identify its physico-chemical properties able to maximise the

534 ammonia removal. The mechanisms for ammonia adsorption on BC from wastewater and

535 digestate have been studied in literature (Table 5), resulting in promising values of

536 ammonium adsorption capacity (up to hundreds of mg NH_4-N g^{-1} BC). Yin et al. (2017)

537 [112] reported that physical sorption could be supported by high SSA and large porous

538 structure. However, various studies suggested that porosity and SSA may not be the

539 predominant factors in ammonium adsorption [154,155]. For instance, ion exchange may

540 occur between acidic functional groups on BC surface and ammonium [112,156,157],

541 and CEC could have a major role in enhancing the ammonium adsorption capacity of BC

542 [157]. Zhang et al. (2014) [158] found that BC derived from pyrolysis of corn cob at 400

543 °C exhibited higher ammonium adsorption capacity than those produced at 600 °C due to

544 the presence of functional groups with higher acidity. Thus, the definition of the proper

545 pyrolysis temperature and the other control parameters is crucial for enhancing the

546 adsorption capacity of BC.

547 In conclusion, various studies reported the potential of BC in alleviating ammonia

548 inhibition (Tables 4 and 5) through different mechanisms. The direct adsorption of

549 ammonia on BC may contribute to the mitigation of ammonia inhibition. However,

550 further studies are required to clarify the effective role of direct mechanisms in complex

551 AD systems in presence of other phenomena, i.e. the close bond between ammonia and

552 VFAs inhibition. In some cases the direct removal of ammonium may not be the main

553 contribution to the mitigation of ammonia inhibition by BC [44,82,153]. Instead, other

554 indirect mechanisms (immobilization and faster acclimation of biomass, DIET) have been

555 suggested in literature and will be discussed in the next sections.

556

557 Table 4. A summary of selected works focusing on ammonia/ammonium inhibition mitigation by BC in AD processes (FAN: free ammonia

558 nitrogen; TAN: total ammonia nitrogen).

Biochar			Anaerobic digestion										Reference
Feedstock	Process: temperature [°C]	Dose of biochar	Substrate	Inoculum	Inoculum to substrate ratio (VS basis)	Temperature [°C]	pH	Critical TAN conc. or as specified [mg L⁻¹]	Critical FAN conc. or as specified [mg L⁻¹]	Ammonia removal by biochar	Results and comments		
Fruitwood	Pyrolysis: 800-900°C	10 g L⁻¹	Glucose solution (6 g L⁻¹)	Granular sludge from AD of paper mill wastewater	1:6	35	7	260 3500 7000	- - -		• ↑ Specified CH₄ prod. rates increased by 18.6%, 10.1% and 23.5% respectively • ↓ Lag phase by 30.4%, 12.7% and 23.8% respectively		[44]
1:2 (v/v) mix: - paper sludge - wheat husks	Pyrolysis: 500°C	6.67% w/w (2 g BC per 30 g inoculum)	-	Meso. AD (TS = 4.05%) + Ammonium carbonate	Only 30 g of inoculum	42	7.66 7.73 7.93 7.84 8.07	1626 2126 3126 4126 6626	- - - - -	2.4 mg TAN g⁻¹ BC 2.0 mg TAN g⁻¹ BC 4.2 mg TAN g⁻¹ BC 4.5 mg TAN g⁻¹ BC 6.8 mg TAN g⁻¹ BC	• No clear effect on biogas production was observed		[41]
Macadamia nut shells	Pyrolysis: 350°C	33.3 g L⁻¹	Food waste (+ water + NaHCO₃)	AD from UASB (SS =34 g	-	Room temperature		1500	-		• ↑ COD removal from 78% without BC to 90% with BC		[43]
Corn stover	Gasification	1.82, 2.55, 3.06, 3.64 g BC g⁻¹ TS sludge	WWTP sludge	Thermo WWTP AD	2:1	55	7.5	1100 (total N)	600 (NH₃-N)		• CH₄ yield, biomethanation rate constant and ↑ max CH₄ prod. rate up to 7.0%, 8.1% and 27.6% respectively • ↑ NH₃-N concentration by 41.5% after AD without BC, while by 0.2-18.1% with BC		[151]
Pine pellets White oak pellets	Gasification	2.49, 4.97 g BC g⁻¹ TS sludge 2.20, 4.40 g BC g⁻¹ TS sludge	WWTP primary sludge TS = 1.25% (inoc +subs)	Meso. and thermo. WWTP AD TS = 1.25% (inoc +subs)	2:1	37, 55	7.2-7.3	750 (total N)	400-450 (NH₃-N)		• ↑ CH₄ yield by 3.9-9.5% • ↑ NH₃-N concentration by 67.0% after AD without BC, while by -7.2 to 4.7% with BC • ↑ CH₄ yield by 5.7-9.6% • ↑ NH₃-N concentration by 67.0% after AD without BC, while by -7.2 to 4.7% with BC		[33]

Corn stover Pine	Gasification: 850°C	0.25, 0.375, 0.5, 1.0 g d^{-1}	Primary sludge + WAS (TS = 7.01%)	WWTP AD from TPAD: 1 stage (TS = 6.14%) 2 stage (TS = 3.77%)	2:1	55	7.4 (stage 1); 5.3-6.0 (stage II)	- -	- -	6.2-13.2% 3.6-11.2%	• ↑ CH$_4$ content by 13.7-25.3% • ↑ CH$_4$ prod. rate by 5.5-36.9% • ↑ CH$_4$ content by 0.7-9.1% • ↑ CH$_4$ prod. rate by -2.3-16.6%	[34]
Wheat bran pellets Coppiced woodlands Orchard pruning	Pyrolysis: 800°C Pyrolysis: 500°C Pyrolysis: 500°C	25 g L^{-1}	Food waste fermentate	Anaerobic methanogenic culture (from WAS AD)	-	20	7.5		200–250 (NH$_3$-N)		• After acclimation: ↑ rate of VFAs degradation and ↓ lag-phase; • No adsorption of ammonia by BC	[45]
Wheat straw	Pyrolysis: 350, 450, 550°C	5% w/w (chicken manure)	Chicken manure (+ water)	Chicken manure meso. AD	Inoculum: 20% of WV of AD reactor	35	Initial: 6.7-7.6	3450-3540 (average)	472-600 (max)		• ↑ Cum. CH$_4$ yield • ↓ TAN compared to control	[82]
Fruit wood	Pyrolysis: 350, 450, 550°C						Initial: 6.7-7.0	3440-3650 (average)	421-634 (max)	up to 25% TAN	• ↑ Cum. CH$_4$ yield up to 69% • ↓ TAN compared to control • ↓ FAN up to 58% compared to control	
Air-dried chicken manure	Pyrolysis: 350, 450, 550°C						Initial: 6.9-7.3	3880-3960 (average)	496-701 (max)		• ↑ Cum. CH$_4$ yield • ↓ TAN compared to control	

559

560

561   Table 5. Ammonium adsorption capacity of different BCs (NA: not available)

Biochar production			Biochar properties					Adsorption				Reference
Feedstock	Pyrolysis temperature [°C]		BET-SA [m^{2}g^{-1}]	pH	CEC [cmol$_c$ kg^{-1}]	Total pore volume [mL g^{-1}]		Source of NH$_4^+$-N	Initial NH$_4^+$-N [mg L^{-1}]	NH$_4^+$ adsorption capacity [mg NH$_4^+$-N g^{-1} biochar]		
Oak wood	400-450		NA	9.9	59.4 ± 8.1	NA		Ammonium solution	1000	100.9 ± 3.4		
Oak wood	-		NA	9.7	105.8 ± 12.1	NA			-	129.4 ± 34.8		
Greenhouse waste	-		NA	10.6	109.5 ± 21.8	NA		-	-	118.2 ± 26.9		
Municipal waste	-		NA	9.5	65.7 ± 16.2	NA		-	-	137.3 ± 0.6		
Presscake from AD	-		NA	10.3	51.0 ± 5.5	NA		-	-	105.8 ± 11.5		[154]
Oak wood	600-650		NA	10.3	76.6 ± 0.7	NA		-	-	114.4 ± 3.4		
Oak wood	-		NA	8.6	65.2 ± 20.2	NA		-	-	123.5 ± 28.7		
Greenhouse waste	-		NA	11.0	146.2 ± 32.3	NA		-	-	99.3 ± 28.5		
Municipal waste	-		NA	10.2	67.9 ± 12.5	NA		-	-	128.3 ± 6.7		
Presscake from AD	-		NA	10.1	52.6 ± 11.5	NA		-	-	136.2 ± 18.1		
Hardwood	600		147.0	9.80	NA	0.176		AD slurry	500–580	114.2		
Corncobs	-		23.0	8.92	NA	0.098		-	-	108.9		[159]
Mixed sawdust	-		6.80	8.60	NA	0.038		-	-	24.7		

Mixed wood	600	273.623	9.80	NA	0.176	Swine manure AD slurry	1400 mg N L^{-1}	44.64 ± 0.602	
Rice husk	/	10.995	7.80	NA	0.038	-	-	39.8 ± 0.54	[155]
1:2 (v/v) mix: - paper sludge - wheat husks	500	NA	NA	NA	NA	During anaerobic digestion	1626 mg TAN kg^{-1}	2.4 mg TAN g^{-1}	
	-	-	-	-	-	-	2126 mg TAN kg^{-1}	2.0 mg TAN g^{-1}	
	-	-	-	-	-	-	3126 mg TAN kg^{-1}	4.2 mg TAN g^{-1}	[41]
	-	-	-	-	-	-	4126 mg TAN kg^{-1}	4.5 mg TAN g^{-1}	
	-	-	-	-	-	-	6626 mg TAN kg^{-1}	6.8 mg TAN g^{-1}	
Fruitwood	800-900	NA	NA	NA	NA	NH$_4$Cl solution	NA	2-3 mg N g^{-1}	[44]

562

563 *4.3. Effects on microbial populations*

564 Many authors reported the positive effects of BC on microbial populations in AD (Table

565 6). In semi-continuous and continuous AD experiments, BC addition improved methane

566 production [34] keeping it stable even with rising OLRs [29,49] and resulted in higher

567 COD removal rates [43,50,51].

568 Although there is a good agreement among the studies in terms of enhancement of AD

569 process performances (11-30 % reduction of lag phases and 11-50 % increments of

570 methane production rates) (Table 6), there is not a common hypothesis to explain BC

571 influence on microbial populations, and different possible mechanisms are proposed as

572 follows.

573 *4.3.1. Microbial attachment and acclimation*

574 Immobilization and acclimation of balanced microbial consortia on various support media

575 are commonly adopted for counteracting various drawbacks of AD processes [160],

576 thanks to the intensification of syntrophic conversion relationships, along with a major

577 resistance to inhibition effects [161]. Wang et al. (2018) [50] found that BC acted as an

578 inert core for microbial aggregation, resulting in a higher microbial growth rate and

579 accelerating sludge granulation. Cooney et al. 2016 [53] investigated the possibility of

580 accelerating biofilm formation by adding BC during the start-up of a packed bed

581 anaerobic digester at pilot scale. In a relatively short time, the AD system reached stable

582 and good performances, suggesting the rapid development of biofilms rich in active

583 methanogens.

584 High SSA, proper porosity structure and particle size, superficial hydrophobicity seemed

585 to be important properties favouring microbial immobilization [12,52]. Further,

586 conductive materials may act as ideal support media due to their surface hydrophobicity

587 and porous structure [54,55]. In particular, macropores can help the attachments of
588 bacterial cells [19,162,163]. Lü et al. (2016) [44] explored the influence of different
589 particle sizes of BC (2-5 mm, 0.5-1 mm, 75-150 μm) on the microbial distribution during
590 the AD of glucose under ammonium stress. They stated that bacteria could access more
591 easily fine particles than coarse particles. As a consequence, the attachment and
592 colonization of microbial populations on BC can limit the risks of wash-out, accelerate
593 the acclimation of microbes during substrate-induced inhibition, reduce the distance
594 between syntrophic bacteria and methanogens, facilitate interspecies electron transfer and
595 exchanges of VFAs or other metabolites [16,36,137]. Li et al. (2018) [46] found that
596 methanogens survived under acidic stress in presence of BC during co-digestion of FW
597 and WAS. Further, the immobilization of microbes could significantly attenuate ammonia
598 inhibition [43,44]. The colonization of porous materials by microbes can alter the
599 dominant species, making them more resistant and more rapidly acclimatized to substrate-
600 induced inhibition [29,36,164]. Magnetic BC favoured the enrichment of acido/acetogens
601 and methanogens absorbed on its surface shortening the microbial contact distance, thus
602 VFAs produced by acido/acetogen bacteria could be more quickly transported to
603 methanogens than in control digesters during AD of OFMSW in batch tests [16,139]. The
604 distance of less than 1 μm has been reported to be essential for the oxidation of VFAs and
605 hydrogen production [19,165].

606 *4.3.2. Selective colonization of functional microbes*

607 The effect of BC addition on microbial communities was investigated with the aim of
608 identifying the most abundant bacterial and archaeal populations and, indirectly, the main
609 interspecies interactions (Table 6). In detail, most studies focused on: biofilm formation
610 [26,48,53]; shifts of microbial populations [28,34,46,47]; selective enrichment of

611 microbial -DIET partners [38,44,49,50]; promotion of DIET [38,44–46,49,51,139]. The

612 relevant anaerobic bacteria and archaea enriched in BC amended digesters are reported

613 in Table 7, together with BC properties, substrate and inoculum used in AD tests. Many

614 bacterial species were found in reactors supplemented with BCs, none of them identified

615 as more recurrent. Among archaeae, most studies identified *methanosaeta*,

616 *methanosarcina*, *methanobacterium*, and *methanolinea* species in BC amended reactors.

617 Different studies [44,48,51] investigated the spatial distribution of bacteria and archaea

618 by dividing sludge samples into different fractions, from suspended to attached to BC. Lü

619 et al. (2016) [44] postulated an explanation for the spatial distribution of methanogens

620 into BC pores by their cell morphology and dimension. The short fibrous form of

621 Methanosaeta (0.8-7 μm in size) could explain its attachment into internal and external

622 pores, while the long fibrous form of Methanobacterium (1.2-120 μm in length) could

623 limit its penetration into BC pores [44,166].

624 *4.3.3. Promotion of syntrophic metabolisms*

625 Many studies (Table 7) suggested that BC addition may improve electron transfer

626 mechanisms between anaerobic bacteria and archaea closely attached to BC surface. The

627 overall AD efficiency depends on effective syntrophic interactions between bacteria and

628 methanogens exchanging electrons to satisfy their energy requirements [56], happening

629 through various routes:

630 - Indirect interspecies electron transfer (IIET) via soluble (i.e. hydrogen, formate,

631   acetate) [167,168] and insoluble (humic substances) [169,170] compounds;

632 - Direct interspecies electron transfer (DIET) via electrical conductive pili, membrane-

633   bound electron transport proteins, and conductive materials (i.e. magnetite, biochar,

634   granular activated carbon, carbon cloth) [171–173].

635 In IIET hydrogen and formate operate as electron shuttles between syntrophic-producing

636 bacteria and consuming-methanogens [56]. Diffusion regulates the transfer of a

637 metabolite between microorganisms, as defined by Fick's Law [174]: the shorter the

638 distance, the higher the flux of metabolites between microbes. Thereby, when cells

639 aggregate the rate of interspecies hydrogen transfer is enhanced by the moment anaerobic

640 bacteria and methanogenic archaea form compact structures acting as an organ [174,175].

641 However, the diffusion of soluble metabolites is considered a relatively slow mechanism

642 of energy and information transfer [173] and hydrogen IET is regarded as a bottleneck in

643 methane production [171]. On the contrary, DIET consists in the formation of an electric

644 current between electron-donating and electron-acceptor microorganisms without the

645 mediation of electron shuttles [56]. DIET could be faster and more specific compared to

646 IIET [173,176]. Park et al. (2018) [171] reported that direct exchange of electrons via

647 conductive pili was observed in co-cultures between *geobacter metalliriducens* and

648 *geobacter sulfurreducens* [176], *methanosaeta harundinacea* [177], or *methanosarcina*

649 *barkeri* [178]. Conductive materials such as magnetite [179], GAC [180], and BC [57]

650 were shown to effectively mediate DIET between syntrophic partners.

651 Based on changes in the microbial community composition, many studies justified the

652 enhancement of AD activity by means of the improvement of hydrogen and formate

653 interspecies transfer mechanisms or, more frequently, by DIET via conductive biochar

654 (Table 7). These findings are usually based on indirect observations, i.e. the enrichment

655 of bacterial and archaeal species able to participate to DIET function as potential partners.

656 Martinez et al. (2018) [47] found an enrichment of homoacetogenic bacteria, as

657 *Clostridium, Eubacterium* and *Syntrophomonas*, and H_2 using methanogens through the

658 analysis of microbial communities in digesting WAS and orange peels with BC,

659 suggesting the formation of co-cultures enhancing methane production. Zhao et al. (2016)

660 [51] observed the selective enrichment on BC of *Geobacter* and *Methanosaeta* during

661 AD of synthetic wastewater with butyrate and propionate in UASB reactors. They

662 suggested that butyrate and propionate could be degraded via DIET in the presence of a

663 conductive material, and they found abundance of *Syntrophomonas* and *Smithella*,

664 concluding that the metabolism via interspecies H_2 transfer for butyrate and propionate

665 degradation was probably present. Wang et al. (2018) [50] showed that the microbial

666 community analysis in a BC amended reactor during AD of synthetic wastewater resulted

667 in the selective enrichment of potential DIET-partners, as *Geobacter* and *Bacteroidetes,*

668 as well as archaea *Methanosaeta* and *Methanosarcina*. They suggested that BC could

669 enhance DIET among electrogenic microbes and archaea, improving the electron transfer

670 characteristics of granular sludge, as well as COD removal and methane yield. Wang et

671 al. (2018) [38] found that the addition of different BC doses increased methane production

672 rate and shortened the lag phase during mesophilic AD of dewatered WAS and FW.

673 According to the authors, BC counteracted the pH decrease due to VFAs accumulation

674 through its buffering capacity, and it seemed to promote DIET.

675 Aside from physical properties as SSA and porosity, favouring microbial colonization,

676 other chemical and conductive characteristics of BC may be crucial in the promotion of

677 electrons transfer. The role of electrical conductivity (EC) of BC in AD has been

678 investigated in literature[59]. EC of digestate has been reported to increase in presence of

679 BC [50,151]. However, the EC of digestate seemed unrelated to the conductivity of BC,

680 which varies depending on the metabolism and composition of microbial species [56].

681 The capability of BC in promoting DIET appeared to be comparable to that of GAC, even

682 if the EC of BC was roughly 1000 times lower [57,171]. Barua and Dhar (2017) [181]

683 reported that multi-species aggregates from anaerobic digesters exhibited conductivity

684 ranging 0.2-36.7 μS cm^{-1}, suggesting its relation with DIET via conductive pili . Martins

685 et al. (2018) [56] stated that conductive materials could have a similar role of humic

686 substances in DIET, acting as electron shuttles by receiving and donating electrons. Wang

687 et al. (2019) [49] suggested that BC from sawdust may act as a temporary electron

688 acceptor for VFAs oxidation during thermophilic AD. They found a significantly higher

689 and more stable methane yield at higher OLR values during anaerobic co-digestion in

690 semi-continuous mode with the addition of BC from sawdust, while they did not show

691 any enhancement of AD with the addition of BC from sewage sludge. The main effects

692 of sawdust BC seemed to be the enhancements of microbial activities and syntrophic

693 oxidation of VFAs. The EC of both BCs was similar, suggesting it was not a determinant

694 factor in the promotion of syntrophic oxidation of VFAs. Instead, the authors speculated

695 that the presence of redox-active phenazine structures in the BC from sawdust could

696 promote VFAs degradation via DIET. Thereby, for better investigating whether BC from

697 sawdust could substitute hydrogen as electron acceptor in syntrophic oxidation of VFAs,

698 they conducted a series of batch experiments with butyrate or propionate as substrates in

699 which methanogenesis was inhibited. The control reactors did not show degradation of

700 butyrate and propionate, while the addition of BC stimulated their oxidation as well as

701 the production of acetate, supporting the hypothesis of the electron-accepting capacity of

702 BC in the syntrophic process.

703 The adoption of a further control in AD tests amended with a non-conductive material

704 can be crucial to investigate whether the stimulatory effects of BC on methane production

705 can be more closely linked to its physical properties (i.e. SSA and porosity) rather than

706 its electrical properties [56]. This was evident in the study of Cruz Viggi et al. (2017)

707 [45], where they introduced two controls without BC and with non-conductive silica sand

708 for AD of FW. They found that VFAs degradation and methane production were faster

709 in the case of BC amended reactors than both the control reactors, suggesting the

710 predominant influence of the electrical properties of BCs.

711 Table 6. A summary of selected works focusing on positive effects of BC on microbial populations in AD processes

Biochar			Anaerobic digestion							References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms		
Sawdust	Pyrolysis: • 500°C • 1 h • 20°C min^{-1}	10 g L^{-1}	Food waste (TS = 94.2 g L^{-1})	WAS (TS = 89.1 g L^{-1})	55°C	Batch V = 120 mL S/I (VS) = 0.25 - 3	By ↑ OLR: • ↓ lag time • ↑ CH$_4$ prod. rate	• ↑ buffer capacity • Microbial attachment and acclimation on BC • Promotion of DIET • Selective succession of microbes		[46]
Pine sawdust	Pyrolysis: • 650°C • 20 min	8.3 - 33.3 g L^{-1}	Food waste (bread) (TS = 61.2%)	WWTP-sludge (heated at 95°C)	35°C	Batch V = 100 mL TPAD	1st phase: • ↓ lag phase • Faster VFAs generation • ↑ H$_2$ prod. rate • ↑ Cum. H$_2$ prod. 2nd phase: • ↓ lag phase (41-45%) • Faster VFA degradation • ↑ CH$_4$ prod. rate	1st phase: • Promotion biofilm formation • Providing temporary nutrients • Buffering pH by BC 2nd phase: • Promotion methanogenic biofilm formation • No buffering pH by BC		[26]
Macadamia nut shells	Pyrolysis: • 350°C • 2 h	33.3 g L^{-1}	Food waste + water + (↑ N-NH$_4$ conc.)	AD from	Room temperature	CIC reactor V = 4.6 L HRT=16 h	• ↑ COD removal by 15%	• ↓ NH$_3$ inhibition by BC • ↑ Alkalinity by BC • ↓ VFAs accumulation		[43]

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
	• 10°C min⁻¹			(SS = 34 g L⁻¹)				• ↑ Selective enrichment of functional microbes • Microbial attachment and acclimation on BC	
Sawdust	Pyrolysis: • 500°C • 1.5 h • 10°C min⁻¹	2 - 15 g L⁻¹	Dewatered WAS + Food waste (TS = 8.8%) + water	Meso. AD from brewery factory (TS = 6.8%)	35°C	Batch Serum bottles WV = 90 mL S/I = 0.75 - 3 (VS)	• ↓ lag phase by 27.5–64.4% • ↑ Max CH$_4$ prod. rate by 22.4%–40.3%	• Buffer capacity by BC (alleviate ↓ pH due to ↑ VFAs) • ↑ DIET by BC (temporary electron acceptor, due to the richness of surface functional groups) • Selective enrichment of microbial DIET-partners by BC	[38]
Sawdust	Pyrolysis: • 500°C	15 g L⁻¹	Food waste + Sewage sludge (TS = 9.2%) FW/Sludge = 4:1 (TS)	Brewery Meso. AD (TS = 5.2%)	55°C	Semi-continuous Serum bottles WV = 150 mL ↓ HRT, ↑ OLR	• ↑ CH$_4$ yield by 16.0%−55.2% • Stable CH$_4$ prod. at ↑ OLRs	• ↑ VFAs syntrophic oxidation by BC • High SA of BC → microbial attachment (?), closer association of syntrophic partners • Electroactive functional groups of BC → stimulation of DIET (?)	[49]
Corn stover	Gasification: • 850°C	0.25 - 1.0 g d⁻¹ (2nd phase)	Primary sludge + WAS (TS = 7.01%)	WWTP AD	55°C	Semi-continuous V = 500 mL TPAD:	• ↑ % CH$_4$ by 13.7-25.3% • ↑ CH$_4$ prod. rate by 5.5-36.9%	• Adsorption and precipitation of CO$_2$ by BC • ↓ TAN • ↑ Alkalinity • ↑ Macro-/micro-nutrients in digestate • Shift in bacterial community	[34,182]

Biochar						Anaerobic digestion			References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				TPAD: 1 ph. (TS = 6.14%) 2 ph. (TS = 3.77%)		1) HRT = 5, 15 d 2) HRT = 13 - 30 d		• Inhibition at high BC doses	
Pine	-	-	-	-	-	-	• ↑ % CH$_4$ by 0.7-9.1% • ↑ CH$_4$ prod. rate by 2.3-16.6%		
Corn stover	Gasification	1.82 -3.64 g BC g^{-1} TS sludge	WWTP sludge	Thermo. WWTP AD	55°C	Batch V = 600 mL 26 days	• ↑ % CH$_4$ (88.5-96.7%) • ↑ CH$_4$ yield	• ↑ buffer capacity • ↑ electrical conductivity in digester (+37%) → ? ↑ extracellular electron transfer • ↓ NH$_3$ inhibition • CO$_2$ sequestration by BC • ↑ macro-/micro-nutrients in digestate	[151]
Rice husks	Gasification: • 900-1000°C	1%, 3% w/w	Cattle manure + water (TS = 5%)	-	35°C	Batch V = 1400 mL	• ↑ Biogas prod. by 31% by 1% BC • ↓ % CH$_4$ by 7% by 1% BC • No benefits by 3% BC	• ? Microbial biofilm formation on BC	[30]

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Rice husks	Gasification: • 900-1000°C	1%, 3% w/w	Cattle manure + water (Mix: TS = 5%)	-	25-30°C	Semi-continuous WV = 12 L HRT = 20 days	• ↑ Biogas prod. by 4-5% by BC • ↓ % CH_4	• ? Not enough time for biofilm formation	[31]
Dry dairy manure	Pyrolysis: • 350°C • 3 h • 10°C min^{-1}	0, 1, 10 g L^{-1}	Dry dairy manure	Inoculum from lagoon, fed with dried manure (TS = 115.85 g L^{-1})	20°C	Batch: Serum bottles V = 280 mL S/I = 1 (VS)	• ↑ CH_4 yield up to 26.5% • ↓ lag phase • ↓ total VFAs	• No biofilm formation on BC (?) • No effects on DIET by BC (?) • ↑ Alkalinity and ↑ pH (buffer capacity)	[27]
-	-	-	-	-	35°C	-	• ↑ CH_4 yield up to 24.9% • ↓ lag phase • ↓ total VFAs	• ↑ Alkalinity and ↑ pH (buffer capacity)	
-	-	-	-	-	55°C	-	• ↑ CH_4 yield up to 24.7% • ↓ lag phase • ↓ total VFAs	• ↑ Alkalinity and ↑ pH (buffer capacity)	
Vineyard prunings	Pyrolysis: • 550°C	10, 30 g L^{-1}	Co-digestion:	WWTP AD	37°C	Batch: • V = 250 mL	Batch: • ↓ lag phase	• Promotion of synthrophic metabolism by BC • Adsorption of inhibitors	[47,183]

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
			• Orange peels (TS = 311g kg^{-1}) • Sewage sludge (TS = 28.7g kg^{-1})	(TS = 35.5 g kg^{-1})		Semi-continuous • V = 3 L • HRT = 10-30 days	• ↑ CH_4 prod. Semi-continuous: • ↑ CH_4 prod.	• Adhesion and growth of microorganisms by BC SA	
Coconut shell	Pyrolysis: • 450°C	1:1 (TS)	Citrus peel (TS = 16.6%)	WWTP AD (TS = 11.0 %)	35°C	Batch V=500 mL S/I = 0.31 - 0.33 (VS)	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC	[40]
Rice husk	-	1:1 (TS)	-	-	-	-	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC • Adhesion and growth of microbes on BC	
Wood	-	1:1; 1:2; 1:3; 2:1 (TS)	-	-	-	-	• ↓ lag phase • ↑ Cum. CH_4 prod.	• Limonene adsorption by BC • Adhesion and growth of microbes on BC	

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Rice straw + FeCl$_3$ (3.2 g FeCl$_3$:100 g rice-straw)	In FeCl$_3$ solution: • 2h Carbonization: • 500°C • 2h	0.5% w/w	OFMSW + water (TS = 1.64%)	OFMSW thermo. AD + water (TS = 2.19%)	35°C	Batch Serum bottles V = 500 mL, S/I = 1 (VS)	• ↓ lag phase • ↑ CH$_4$ prod. by 11.69%	• No effects on NH$_3$ by BC • No effects on pH by BC • ↑ syntrophic associations of bacteria on BC • (?) DIET by high conductivity of BC	[139]
Rice straw	Carbonization: • 500°C • 2h	-	-	-	-	-	• ↓ lag phase • ↓ CH$_4$ prod.	• No effects on NH$_3$ by BC • No effects on pH by BC	
Cow manure	Pyrolysis: • 500°C • 4 h • 100°C h^{-1}	2 – 14 g L^{-1}	Dry beer lees (TS = 62.5%)	Meso. WWTP AD (TS = 36.7%)	35°C	Batch WV = 150 mL TS = 25% S/I = 3 (TS)	• ↓ lag phase • ↑ Max cum. CH$_4$ prod. up to 82.9%	• Promotion of DIET by BC conductive properties (?) • Microbial colonisation and biofilm formation on BC (?) • ↑ Alkalinity and ↑ pH (buffer capacity) • Selective enrichment of methanogens by BC	[28]
-	-	-	-	Thermo. WWTP AD (TS = 38.5%)	55°C	-	• ↓ lag phase • ↑ Max cum. CH$_4$ prod. up to 47.2%	-	
Rice straw	Pyrolysis: • 500°C	4 g L^{-1}	Synthetic wastewater	WWTP sludge	35°C	UASB	UASB: • ↑ COD removal rate	• No effects on pH by BC • BC inert core for microbial aggregation	[50]

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				(SS = 25.2 g L⁻		• Continuous mode • V = 5500 mL • HRT = 12 h, 12-6 h Batch • Serum bottles • V = 550 mL	• ↑ VFAs degradation • ↑ gran. sludge conductivity and quality Batch: • ↓ lag phase by 28.6% • ↑ biogas yield • ↑ %CH₄	• Selective enrichment of microbial DIET-partners by BC	
-	Biochar	-	Grease trap waste wastewater (TSS = 1.04 g L⁻¹)	-	37°C	Biochar packed bed anaerobic digester • V: 900 L +1500 L+ 1500 L • ↓ HRT (3.1 – 1.8 days)	• COD removal:68% • Total VFAs: from 4.7 (feed) to 1.46 g L⁻¹ (effluent) • %CH₄ > 60% • Start-up: 59 days	• ↑ Methanogenic biofilm communities on BC • BS as packing material for growth and retention of biofilm	[53]

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
Wheat bran pellets	Pyrolysis: • 800°C • 3h	25 g L^{-1}	Food waste fermentate	Methanogenic culture (from WAS digestate)	20°C	Batch V = 120 mL	After acclimation: • ↑ rate of VFAs degradation • ↓ lag-phase	• No effects on pH via BC • No effects on NH_3 via BC • Promotion of IET by BC	[45]
Coppiced woodlands	Pyrolysis: • 500°C	-	-	-	-	-		-	
Orchard pruning	Pyrolysis: • 500°C	-	-	-	-	-		-	
Fruitwood	Pyrolysis: • 800-900°C	10 g L^{-1}	Glucose (6 g L^{-1})	AD gran.	35°C	Batch Serum bottles	• ↓ lag phase by 5.9-23.9% • ↑max CH_4 prod. rate by 23.5-47.1% • Faster VFAs degradation	• NOT NH_4 adsorption • NOT ↑ buffer capacity • DIET promotion via BC • Affinity of methanogens with BC	[44]

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
				Ammonium: 0.26, 3.5, 7 g-N L^{-1}					
Fruit wood	Pyrolysis: • 800°C	10 g L^{-1}	Nutrient solution + glucose (2 - 8 g L^{-1})	Meso. pulp sewage digestate (1 g VS L^{-1})	35°C	Batch Serum bottles V = 500 mL	• ↓ lag phase by 11.4-30.3% • ↑ Max CH_4 prod. rate by 5.2-86.6% • ↑ VFAs production and degradation	• Selective colonization of functional microbes by BC • Not ↑ buffer capacity • ? Biofilm growth on BC • ? Promotion of DIET or Hydrogen IET by BC	[48]
Pine wood	Pyrolysis: • 600°C • 2h	5 g L^{-1}	Synthetic wastewater with butyrate	WAS digestate (TSS = 13.1 g	37°C	UASB WV = 1000 mL	• ↑ CH_4 prod. rate by 25% • ↑ COD removal	• ↑ Butyrate degradation via DIET in UASB via BC • Selective enrichment of microbial DIET-partners by BC	[51,57]
			Synthetic wastewater with propionate				• ↑ CH_4 prod. rate by 16% • ↑ COD removal	• ↑ Propionate degradation via DIET in UASB via BC • Selective enrichment of microbial DIET-partners by BC	

Biochar			Anaerobic digestion						References
Feedstock	Production	Dose of biochar	Substrate	Inoculum	Temperature [°C]	Experimental mode	Results	Possible mechanisms	
-	Biochar	2.5 g L^{-1}	Synthetic wastewater with ethanol	WAS digestate (TSS = 13.1 g	37°C	UASB WV = 1000 mL ↓ HRT (24 - 8 h)	• ↑ COD removal: ≥ 93% (control: 75-83%) • ↑ CH$_4$ prod. rate	• (?) Promotion syntrophic metabolism via DIET with BC in UASB reactors	[29]

CIC: controlling internal circulation; COD: chemical oxygen demand; DIET: direct interspecies electron transfer; FW: food waste; HRT: hydraulic retention time; IET: interspecies electron transfer; OLR: organic loading rate; OFMSW: organic fraction of municipal solid waste; SA: surface area; S/I: substrate to inoculum ratio; SMP: specific methane potential; SS: suspended solids; TPAD: two phased anaerobic digestion; TSS: total suspended solids; UASB: up-flow anaerobic sludge blanket; VFA: volatile fatty acid; WAS: waste activated sludge; WWTP: wastewater treatment plant; WV: working volume; V: volume.

712

713

714 Table 7. A summary of studies reporting the selective enrichment of bacteria and archaea by BC addition during AD processes

Biochar production		Biochar properties			Anaerobic digestion					Reference
Feedstock	Pyrolysis temperature [°C]	BET-SSA [m^2g^{-1}]	Electrical conductivity [$S\ m^{-1}$]	Total pore volume [$cm^3\ g^{-1}$]	Temperature [°C]	Substrate	Identification technique	Enriched Bacteria	Enriched Archaea	
Wheat bran pellets	800	55 ± 1	49.9	0.0445	20	Food waste fermentate	FISH- CLSM		More Methanosarcina-like Archaea rather than Methanosaeta like Archaea	[45]
Coppiced woodlands	500	61 ± 1	1.6	0.0483						
Orchard pruning	500	13.7 ± 0.5	0.5	0.0165						
Macadamia nut shells	350	12.7	-	-	Room temperature	Food waste + water	16S rRNA sequencing	Bacteroidales Anaerolineales Syntrophobacterales	Methanoregulaceae Methanotrichaceae Methanobacteriaceae	[43]
Fruitwoods	800-900	-	-	-	35	Glucose	16S rRNA sequencing	Enterobacteriaceae	Methanobacterium Methanosaeta Methanosarcina	[44]
Fruit wood	800	-	-	-	35	Glucose	16S rRNA sequencing	Syntrophomonas Clostridium Clostridiaceae	Methanobacterium Methanosaeta Methanosarcina	[48]
Rice straw + $FeCl_3$ (3.2 g $FeCl_3$:100 g rice-straw)	500	51.14	-	0.0328	35	OFMSW + water	16S rRNA sequencing	Bacteroides Clostridiaceae Porphyromonadaceae Moraxellaceae	Methanosarcina Methanobacterium OTU in Methanomicrobiales Methanosaeta	[139]
Rice straw	500	111.5	-	-	35	Synthetic wastewater	16S rRNA sequencing	Bacteroidetes unclassified (23.65%) Bacteroidales unclassified (9.19%)	Methanosaeta (77.18%) Methanosarcina (11.65%)	[50]

								Treponema (6.43%)		
								Smithella (5.56%)		
								Brooklawnia (5.45%)		
								Geobacter (5.42%)		
Sawdust	500	248.6	-	-	35	Dewatered WAS + food waste + water	16S rRNA sequencing	Anaerolineaceae Porphyromonadaceae	Methanosaeta Methanobacterium Methanolinea	[38]
Cow manure	500	112.6	-	0.0156	35	Dry beer lees	16S rRNA sequencing	Chloroflexi Bacteroides Proteobacteria	Methanospirillum Methanosarcina Methanolinea	[28]
Vineyard prunings	550	240 ± 4.8	-	-	37	Orange peels	16S rRNA sequencing	Bellilinea Trepomena Clostridium Petrimonas Proteiniphilum Bacteroides	Methanosaeta Thermogymnomonas Methanolinea Methanofollis	[47]
Vineyard prunings	550	240 ± 4.8	-	-	37	Sewage sludge	16S rRNA sequencing	Clostridium Longilinea Curvibacter Eubacterium Syntrophomonas	Methanosaeta Methanolinea Thermogymnomonas Methanobacterium	
Pinewood	600	209.33 µS cm^{-1}	-	-	37	Synthetic wastewater with butyrate	16S rRNA sequencing	Attached sludge: Geobacter Thermanaerovibrio Syntrophomonas	Attached sludge: Methanosaeta Methanosarcina Methanospirillum	[51]
Pinewood	600	209	4.33 µS cm^{-1}	-	37	Synthetic wastewater with propionate	16S rRNA sequencing	Attached sludge: Geobacter Smithella	Attached sludge: Methanosaeta Methanobacterium	

51

								Syntrophus	Methanosphaerula	
Biochar	-	-	-	-	37	Grease trap waste wastewater	16S rRNA sequencing	Attached to BC: Aminobacterium Syntrophomonas Sporanaerobacter Escherichia	Attached to BC: Methanobacterium Methanosarcina Methanobrevibacter	[53]
Sawdust	500	248 ± 34	-	-	55	Food waste	16S rRNA sequencing	Coprothermobacter (36.3%) Fervidobacterium (20.0%) Syntrophothermus Treponema	Methanosaeta (43.9%) Methanosarcina (15.8%)	[46]
Corn stover	850	315.2	-	0.09	55	Primary sludge + WAS	16S rRNA sequencing	Firmicutes (Clostridia) Bacteroidetes Proteobacteria	Methanothermobacter (>90%) Methanosarcina	[34]
Pine		353.1	-	0.23						
Sawdust	500	248.6 ± 9.4	0.11 µS cm^{-1}	-	55	Food waste + Sewage sludge	16S rRNA sequencing	Defluviitoga Tepidimicrobium	Methanothermobacter Methanosarcina	[49]

NA: not available; CLSM: confocal laser scanning microscopy; FISH: Fluorescence in situ hybridization; OFMSW: organic fraction of municipal solid waste; SSA: surface area; WAS: waste activated sludge.

715

716

717   *4.4. Effect of biochar on digestate quality*

718   Anaerobic digestate has been considered as soil improver because it is rich in nutrients

719   [184–186]. However, challenges related to digestate management have recently grown in

720   association with EU regulations on ammonia, volatile organic acids, phenolic

721   compounds, heavy metals, PAHs and PCBs [4,187]. So far, most technologies available

722   to exploit digestate as soil improver are based on mechanical/physical (e.g. mechanical

723   dewatering, semipermeable membranes and evaporation) or chemical processes (e.g.

724   ammonia stripping and nutrients adjustment) (Table 8).

725

726   Table 8. Advantages and disadvantages of conventional technologies for digestate

727   processing [188–191].

Methods	Advantages	Disadvantages
Solid-liquid separation	Rich in phosphorus and suitable for fertilizer application	Liquid fraction has been considered as a surface and ground water pollutions
Belt and drum dryers	treatment and upgrading of digestate to a solid or concentrated product	Rapid volatilization of ammonium causes severe ammonia emission
High-Tech technologies (e.g. ammonia stripping, membrane process and vacuum evaporation exist)	Production of several streams with different physical and chemical properties.	Expensive
Mixing solid digestate with desired nutrient	Increasing value per ton	-

728

729   Dehydrated digestate could be used in non-agricultural markets as a heating fuel,

730   however, this use implies nutrient and metal losses, which in turn have negative impacts

731 on the environment and crops. Consequently, three approaches have been conventionally

732 applied to reduce diffuse pollution resulting from digestate application to land [19,188]:

733 - Nutrient recovery from digestate;

734 - Carbon to Nitrogen ratio adjustment;

735 - Increasing of nutrient retention capacity using an additive.

736 One of the key aspects that should be considered when supplying additives to AD process

737 is their effects on the quality of digestate for subsequent uses, especially as soil improver.

738 Despite literature has not explored enough the fate and properties of digestate with BC to

739 land applications, some potential benefits of BC amendment can be identified as follows.

740 BC remaining in digestate after AD acts as a nutrient retention improver and catalyst,

741 mitigates leaching of heavy metals and pollutants via physical and chemical absorption

742 of organics, phosphate, ammonium, nitrate, nitrite, metals and CO_2 [19,192]. The

743 improvements on digestate quality can be related to BC features as SSA, surface

744 functional groups, ash content and presence of metals (Table 9).

745

746 Table 9. Biochar properties able to improve digestate quality

Factors	Function	Literature	Reference
Textural properties (surface area, pore size)	Higher content of functional group (e.g. Si–O–Si, O–H and C=O)	HCl, $NH_3 \cdot H_2O$ and $KMnO_4$ modification were performed to obtain functional biochar from Swine manure digestate.	[193]
	Increase of the pH and cation exchange capacity	H_2O_2 and KOH modification were performed to obtain functional biochar from domestic sewage sludge digestate	[104]
Ash content	Alkali and alkaline earth metals increase the alkalinity	Pinewood and white oak biochars made digestate a great alternative to agricultural lime fertilizer.	[33]

Metals on the surface	The cation form of the metal can bind with soluble phosphorus	Ex: $3Fe(OH)_2 + 2H_3PO_4^{3-} \rightarrow Fe_3(PO_4)_2 + 6H_2O$	[151]
Functional group	Negatively charged functional groups forms complexes with heavy metals	Manganese oxide-modified biochar composite derived from corn straws improved heavy metal stabilization in the digestate	[194]

747

748 BC supplement in digesters may be beneficial to the fertilizer value of digestates. Shen et

749 al. [34,151] have found that BC addition can cause a substantial increase of the macro-

750 and micro-nutrients as N, P, K, Ca, Mg, and Fe in digestate. Zhang et al. (2020) [195]

751 reported a similar rise of nutrient content in digestate amended with BC, even if

752 concentrations of certain nutrients did not fully meet limits of EU regulation on fertilizing

753 products (Regulation EU 2019/1009). Research has shown that the joint amendment of

754 BC and anaerobic digestate can reduce atmospheric greenhouses emissions from fields,

755 such as N_2O [196] and CO_2 [197–199]. A mixture of dried anaerobic digestate and BC

756 may be an alternative to standard formulations in horticultural potting media [200]. In

757 addition, BC may contribute to improve the composting of digestate [153,201,202],

758 particularly in terms of process performance, compost quality and its benefits on plants

759 [203–205].

760 Further research is needed to understand interactions between BC, digestate and soil for

761 the potential use of the mixture as soil improver after AD. Future studies about the use of

762 BC as additive in AD should also consider its effects on the agronomic value of anaerobic

763 sludge (i.e. content in macro- and micro-nutrients, germination and phytotoxicity tests,

764 and others [206]).

765   *4.5. Effects on biogas upgrading*

766   Raw biogas from AD consists mainly of CH_4 (50-70 % v/v) and CO_2 (30-50 % v/v), along

767   with minor compounds as water vapour, H_2S, NH_3, O_2 and N_2 [207]. Upgrading and

768   cleaning biogas are required to meet the requirements and standards for engines and

769   pipelines, although they represent energetic and economic costs up to 55 % of the total

770   biomethane production cost [33,208,209]. To date, conventional technologies involve

771   water scrubbing, cryogenic separation, physico-chemical absorption, and membranes,

772   among the others [210,211]. Recently, BC has been investigated as adsorbent of CO_2 and

773   H_2S for in-situ and ex-situ applications, as addressed in the following paragraphs.

774   *4.5.1. In-situ biogas upgrading*

775   A series of studies [24,33,34,151] investigated the feasibility of in-situ biogas upgrading

776   by the addition of BC, obtaining methane contents up to pipeline quality (Table 10). Shen

777   et al. (2015) [151] investigated the possibility of sequestering CO_2 with BC during

778   thermophilic AD of WAS for in-situ biogas cleaning and upgrading. They reported

779   average methane contents of 88.5-96.7 % in BC amended reactors, compared to 67.9 %

780   in control reactor, reaching CO_2 removals of 54.9-86.3 % and residual H_2S content below

781   5 ppb. They suggested that CO_2 removal could be promoted by the high porosity of BC,

782   by the large SSA rich of basic sites and of hydrophobic sites. Shen et al. (2016) [33]

783   assessed the AD of WAS with the addition of two woody BCs. They observed average

784   methane content up to 92.3 % and 79.0 % in biogas from BCs amended reactors in

785   mesophilic and thermophilic conditions compared to control reactors, corresponding to

786   CO_2 removals by up to 66.2 % and 32.4 %, respectively. They stated that both BCs owned

787   desirable properties for CO_2 sequestration, and in particular high values of: SSA, porosity,

788 chemical stability, degree of carbonization and alkaline nature. Linville et al. (2017) [24]

789 investigated the influence of particle size and dose of BC from walnut shell on AD of FW

790 in mesophilic and thermophilic conditions. They found higher CO_2 removals compared

791 to control reactors in the case of smaller particle size of BC (61.0 %) than coarse one

792 (51.0 %), due to the larger SSA and ash content. However, according to other studies

793 [33,151], they observed a reduction of methane production with higher BC doses,

794 concluding that this could lead to inhibition caused by higher concentrations of cations

795 released by the BC. Shen et al. (2017) [34] studied the effects of two BCs from corn stover

796 and pine wood on AD of WAS in two-stage digesters. They reported an average methane

797 content of 81.0-88.6 % in the reactor with BC from corn stover and 72.1-76.6 % with BC

798 from pine wood, compared to around 70.0 % for the control. They stated that BCs would

799 release base cations sequestrating CO_2 by chemical sorption and forming

800 bicarbonate/carbonate salts, and that its surface structure would help CO_2 adsorption.

801 Apart from CO_2 adsorption on BC, the major formation of CH_4 depends on the stronger

802 syntrophic cooperation between organic acid-oxidising bacteria and CO_2 reducing

803 methanogens [36,58], underlying the key role of efficient interspecies electron transfers.

804 Further confirmation by other authors to the attractive findings about biogas in-situ

805 upgrading by BC would be beneficial.

806 *4.5.2. Ex-situ biogas cleaning and upgrading*

807 The use of BC and other carbonaceous adsorbents for CO_2 capture from various gaseous

808 streams recently attracted a growing attention [212–214]. Considering ex-situ

809 applications of BC for biogas upgrading and cleaning, Table 11 shows CO_2 and H_2S

810 adsorption capacity of different BCs. Clearly, the adsorption capacity for both CO_2 and

811 H_2S is in a wide range, 0.4-2.3 mmol g^{-1} and 0.2-19.1 mmol g^{-1} respectively. Most of the

812   studies regarding CO_2 capture do not specifically focus on biogas, investigating different

813   BCs eventually subjected to activation. Sethupathi et al. (2017) [215] assessed the

814   adsorption of CH_4, CO_2 and H_2S in a synthetic biogas stream by four BCs in fixed bed

815   adsorbers during continuous experiments. They reported that just CO_2 and H_2S were

816   captured by BCs, which exhibited adsorption capacities up to 0.208 mmol g^{-1} for H_2S and

817   0.126 mmol g^{-1} for CO_2. Creamer et al. (2014) [216] investigated the adsorption of CO_2

818   into BCs from bagasse and hickory wood. They found that BC could effectively capture

819   CO_2 (adsorption capacity up to 73.55 mg g^{-1} or 1.67 mmol g^{-1}), suggesting the importance

820   of surface area and superficial nitrogen groups in CO_2 sequestration, mainly through

821   physical adsorption. Creamer and Gao (2016) [217] reported that the main mechanism

822   for CO_2 sequestration by BC is physical adsorption, suggesting the importance of high

823   SSA [100], adequate pore size (0.5-0.8 nm) [218] and pore volume, thanks to Van der

824   Waals and electrostatic forces. However, the adsorption of CO_2 can also be influenced by

825   BC chemical properties, such as the presence of basic surface functional groups or alkali

826   and alkaline earth metals, hydrophobicity and non-polarity [214]. For instance, Xu et al.

827   (2016) [219] found that the adsorption of CO_2 by three BCs during batch equilibrium tests

828   was due to the presence of alkali and alkaline earth metals (Ca, Fe, K, Mg) by CO_2

829   mineralogical reactions together with physical sorption. Activation and surface treatments

830   of BCs can provide high surface area and micropores for physical sorption and enrich

831   surface functional groups and metal oxides for chemical sorption, leading to remarkable

832   CO_2 adsorption capacities (5.0-7.4 mmol g^{-1}) [220].

833   Other studies applied BC for removing H_2S from biogas (Table 11). Sahota et al. 2018

834   [221] found 84.2 % removal of H_2S from biogas with BC from leaf waste. Kanjanarong

835   et al. (2017) [222] obtained a removal of 98 % of H_2S (8.02 mmol g^{-1}) from biogas with

836 BC, suggesting carboxylic and hydroxide radical groups as responsible of H$_2$S adsorption.

837 Finally, Pelaez-Samaniego et al. (2018) [37] found that BC from AD digestate could

838 effectively remove H$_2$S from a synthetic biogas, possibly facilitated by the presence of

839 ash, porosity, or aromatics in BC. In contrast with CO$_2$ for which adsorption onto BC

840 seemed to be mainly physical, absorption of H$_2$S seemed to involve many chemical

841 mechanisms with BC surface [223].

842 Overall, biochar seems to be a promising adsorbent for ex-situ biogas cleaning and

843 upgrading applications. However, additional studies [215] should focus on the adsorption

844 of CO$_2$ and H$_2$S along with NH$_3$ from real or synthetic biogas, considering their

845 competitive adsorptions, along with the influence of water vapour and the eventual

846 removal of CH$_4$.

847

848 Table 10. Physic-chemical properties of biochars used in biogas in-situ upgrading

Feedstock	Production temperature [°C]	BET-SA [m^{2}g^{-1}]	Total pore volume [cm^{3}g^{-1}]	Average pore diameter [nm]	H/C [molar ratio]	O/C [molar ratio]	Ash [% wt]	Reference
Corn stover	Gasification	315.30	0.09	6.50	0.075 ± 0.007	0.004 ± 0.001	45.18 ± 0.40	[34,151]
Pine pellets	Gasification	310.19	0.19	5.07	0.078 ± 0.009	0.249 ± 0.014	18.69 ± 0.44	[33,34]
White oak pellets	Gasification	296.81	0.15	4.92	0.109 ± 0.026	0.051 ± 0.010	34.90 ± 0.65	
Walnut shell	Gasification: 900 °C	86.5	0.16	7.06	0.20 ± 0.01	0.06 ± 0.01	43.2 ± 0.2	[24]

849

850 Table 11. Biochar adsorption capacity (mmol g^{-1}) of H$_2$S and CO$_2$ during ex-situ

851 applications.

Feedstock	Pyrolysis/activation	Surface area [m^{2}g^{-1}]	Total pore volume [cm^{3}g^{-1}]	Gas	Inlet H$_2$S or CO$_2$ concentration [ppm]	H$_2$S Adsorption capacity [mmol g^{-1}]	CO$_2$ Adsorption capacity [mmol g^{-1}]	Reference

AD digestate fibres	PY/500°C/60 min	134	0.037	Synthetic biogas	2000	3.96 [a]		[37]
	PY/600°C/60min	142	0.035	Synthetic biogas	2000	15.90 [a]		
	PY/600°C/60min +Na$_2$CO$_3$	-	-	Synthetic biogas	2000	19.13 [a]		
Biomass from black liquor	C/450°C/6min	60		N$_2$+H$_2$S	1000	2.14 [a]		[224]
Pig manure	PY/500°C/4hours	47.4		Air + H$_2$S	1% (v/v)	1.75 [a]		[225]
Sewage sludge	PY/500°C/4hours	71.6		Air + H$_2$S	1% (v/v)	1.29 [a]		
Potato peel waste	C/500°C/5min	63		N$_2$ + H$_2$S	1000	1.56 [a]		[226]
Camphor	PY/400°C/5hours	20				3.21 [a]		[227]
Rice hull	PY/400°C/5hours	115				11.23 [a]		
Bamboo	PY/400°C/5hours	58				9.88 [a]		
80% wood chips 20% AD digestate	PY/600°C			Biogas	1020	8.02 [a]		[222]
Perilla leaf	PY/700°C	473.4	0.1	Synthetic biogas		0.537	2.312	[215]
Korean oak	PY/400°C	270.8	0.1	Synthetic biogas		0.178	0.597	
Japanese oak	PY/500°C	475.6	0.2	Synthetic biogas		0.167	0.379	
Soybean stover	PY/700°C	420.3	0.2	Synthetic biogas		0.308	0.707	
Sawdust	G/850°C	182.04	0.0036	N$_2$/CO$_2$			1.08 [b]	[228]
	G/850°C + monoethanolamine	3.17	0.0070	N$_2$/CO$_2$			1.02 [b]	
Sugarcane bagasse	PY/600°C	401.00					1.67 [b]	[216]
Whitewood	PY/500°C + steam activation	840	0.55	He/CO$_2$	30 % mol		1.34 [b]	[229]
Whitewood	PY/500°C + CO$_2$ activation	820	0.45	He/CO$_2$	30 % mol		1.43 [b]	
Whitewood	PY/500°C + KOH activation	1400	0.62	He/CO$_2$	30 % mol		1.77 [b]	
Walnut shell	C900°C/1.5hours	397	0.198				1.65 [b]	[230]
Pig manure	PY/500°C/4hours	31.57	0.044	N$_2$/CO$_2$			0.53 [b]	[219]
Wheat straw	PY/500°C/4hours	20.20	0.041	N$_2$/CO$_2$			0.78 [b]	
Sewage sludge	PY/500°C/4hours	10.12	0.022	N$_2$/CO$_2$			0.41 [b]	

5. Economic and environmental assessments

An economic and environmental evaluation of BC production and application in AD was performed, considering specifically four perspectives: 1. BC production according to feedstock composition and 2. to pyrolysis process conditions; 3. BC application in AD compared to current state of the art technologies addressing AD challenges; 4. integration of AD and pyrolysis processes (to our knowledge, specific studies related to the economic and environmental assessment of BC use in AD processes are not available).

5.1. Economic assessment

Considering BC production, the key parameters to evaluate the economic benefits of feedstocks (perspective 1) are: ash and lignin contents and O/C ratio, which affect pyrolysis yield, molecular weight of bio-oil and BC amount production [231]. Li et al. (2017) [232], based on regression model applied to 346 lignocellulosic feedstocks, stated that higher ash content increases BC production in a range of 12.5-15.5 %, reducing bio-oil production, and consequently the incomes coming out from bio-oil trade, which makes pyrolysis economically profitable. With lower ash content and higher O/C ratio of feedstocks, higher biofuel yields are produced, which leads to better economic performance, in fact minimum fuel selling prices for lignocellulosic feedstocks ranged from 0.53-1.1 Euro/L.

Considering the pyrolysis process (perspective 2), the investment costs for BC production from lignocellulosic feedstocks are: 43 % for pre-treatment and pyrolysis, 35 % for H_2 generation and 22 % for cooling and fractionations [232]. The average operating cost varies from 0.68 Euro/L for woody biomass to 0.86 Euro/L for straw biomass, due to the higher costs of disposal and pre-treatment of straw biomass, respectively 32 % and 34 %

875 of total operational costs [233]. Based on the economic analysis performed by Harsono

876 et al. (2013) [234] and Sahoo et al. (2019) [235], the investment and operational costs

877 related to BC production from lignocellulosic feedstock can only be balanced by a BC

878 trade price of 470 Euro/t.

879 Considering perspective 3, the need to enhance AD feasibility and applicability to

880 unconventional substrates implied higher costs, which should be exceeded by the

881 increased methane production and therefore by the additional electric energy potentially

882 associated. Inorganic and biological additives as iron, micronutrients and ash are

883 conventionally employed to reduce inhibition and facilitate organic matter solubilisation,

884 thus improving methane production. Nevertheless, the application of additives in AD

885 accounts as 3.60-4.10 euro/L of enzyme and as 13-16 euro/L of nutrients [236]. The

886 overall costs of BC, depending on feedstock, pyrolysis process and activating agent

887 (Table 12), could range from 0.2 to 0.5 USD/kg, making BC cheaper than granular

888 activated carbon (GAC), which has production costs ranging between 0.6 and 20 USD/kg.

889

890 Table 12. Comparison of granular activated carbon (GAC) and biochar (BC) production

891 costs depending on feedstock, production process and activating agent

Additive	Feedstock	Production process/ Activating agent	Location	Cost of production (USD kg^{-1})	Reference
GAC	Poultry litter derived carbon	Steam	USA	1.44	[237]
GAC	Rice bran	NaOH	China	3.58-3.77	[237]
GAC	Red oak wood	Steam	USA	0.62-1.27	[237]
GAC - commercial	-	-	USA	1.19-16.34	[237]
GAC	Fruit processing waste	Steam	Malaysia	1.67	[237]
GAC	Rice bran	CO_2	Brazil	3.54	[237]

GAC	Acid treated rice bran	CO_2	Brazil	20.45	[237]
GAC	Wood	KOH	-	2.49	[237]
GAC	Charcoal	KOH	-	1.25	[237]
GAC	Lignite	KOH	-	2.18	[237]
GAC - commercial				1.93	[237]
BC	Empty fruit bunches	Slow PY	Malaysia	0.533	[234]
BC	Straw	Slow PY (large scale)	UK	0.203	[18]
BC	Straw	Slow PY (medium scale)	UK	0.447	[18]
BC	Straw	Slow PY (small scale)	UK	0.351	[18]
BC	Short rotation coppicing, forestry residues, short rotation forestry	Slow PY (large scale)	UK	0.266	[18]
BC	Short rotation coppicing, forestry residues, short rotation forestry	Slow PY (medium scale)	UK	0.500	[18]
BC	Short rotation coppicing	Slow PY (small scale)	UK	0.434	[18]
BC	Forestry residue	Slow PY (large scale)	UK	0.345	[18]
BC	Forestry residue	Slow PY (medium scale)	UK	0.584	[18]
BC	Arboricultural arisings	Slow PY (small scale)	UK	0.213	[18]
BC	Pine wood	Slow PY	USA	0.220-0.280	[238]
BC	-	-	European market (2014)	0.662-0.811[a]	[239]
BC	-	-	-	0.207	[239]
BC	-	-	-	0.600	[68]
BC	-	-	Global, market price (mean)	2.06	[240]
BC	-	-	USA, market price (mean)	2.48 (0.08-13.48)	[241]

GAC: granular activated carbon; PY: pyrolysis.
(a) exchange rate USD/euro (January 2014): 1.3516

892

893   Still considering perspective 3 and moving from the additive's cost to the improvement

894   of AD performances,

895   The economic benefits of the integration of AD and pyrolysis technologies (perspective

896   4) has been explored by literature. The integrated technologies of AD of waste biomass

897   and pyrolysis of the digestate could increase the net electricity production respect to AD

898   alone [80] and enhance its quality as soil amendment [81] with economic and

899   environmental benefits [242]. However, up to date, there is uncertainty regarding the

900   balance between input costs of BC supplementation and output of energy production from

901   AD. Qiu et al. (2019) [59] proposed the energy input-output LCA method to estimate the

902   total energy input for biogas production, by calculating the energy associated with each

903   component used in AD, and the actual energy return of investment. Zhang et al. (2020)

904   [243] investigated the addition of woody BC to improve the thermophilic AD of FW.

905   They concluded that BC supplementation could be economically feasible to enhance

906   thermophilic AD of FW.

907   *5.2. Environmental assessment*

908   Considering feedstocks (perspective 1), life cycle analysis (LCA) from cradle to cradle

909   of the pyrolysis of lignocellulosic feedstocks stated that GHG emissions for husk/shell/pit

910   ranged from 120-250 g CO_2eq/MJ, while for other organic waste, wood and straw they

911   ranged between 20-50 g CO_2eq/MJ [232]. This difference was due to the dominant

912   contribution of indirect land use change from food production. Feedstocks having higher

913   O/C ratio and $0 - 2$ % ash content increased the GHG emissions [244]. Based on GREET

914   database [245], GHG emissions reduction for lignocellulosic feedstocks was 85 - 98 %

915   compared to the GHG emissions for petroleum fuels refining, which was equal to 93

916   gCO_2eq/MJ. GHG emission reductions for lignocellulosic feedstocks satisfy the 50 %

917   share of renewable fuel standard for GHG emission reduction requirement for advanced

918   fuels [246].

919   Considering BC production process (perspective 2), LCA from cradle to gate showed that

920   BC produced from palm oil empty fruit bunches through slow pyrolysis had an energy

921   content higher than the energy required for producing BC [234]. Furthermore, LCA

922   cradle-to grave proved the positive energy balance of BC produced from different

923   lignocellulosic materials [247]. Hence, the positive energy balance of BC production and

924   application, due to the high-energy content of lignocellulosic feedstocks, represents a

925   crucial benefit both from economic and environmental perspectives. One of the main

926   issue of BC produced from renewable feedstocks as lignocellulose wastes (i.e. WAS,

927   wood) and not from purpose grown feedstocks is the higher risk of having contaminants

928   as heavy metals or organic compounds like dioxins, PAHs and PCBs [248].

929   Still considering BC process production (perspective 2), pyrolysis and gasification were

930   compared from the perspective of carbon equivalent abatement (CA): pyrolysis achieved

931   the highest CA, ranging from 0.07 to 1.25 t CO_2 eq/t feedstock, as cardboard and wood

932   waste, while gasification reached the highest electricity generation outputs with 0.9

933   MWhe/t of feedstocks [249]. Activation was proven to represent a high item cost both in

934   terms of economic and environmental perspectives [250]. BC chemical activation costs,

935   in line with non-renewable GAC activation, range between 1.38 and 1.48 Euro/kg,

936   respectively with acidic and basic treatments [251].

937   However, perspective 2 could also be explored considering the existing literature related

938   to the conventional applications of BC as soil improver, adsorbent for water and air

939   pollutants, catalyst for syngas upgrading and biodiesel production (Table 13). LCA

940 studies from cradle-to-grave of conventional BC applications measured in all cases

941 positive environmental benefits compared to conventional perspectives. BC produced

942 from waste forestry feedstock and applied as soil improver contributed to GHGs emission

943 reduction up to 2.74 kg CO_2 eq/ kg BC for the impact categories climate change (CC),

944 natural gas avoided for fossil depletion (FD) and urea avoided for freshwater

945 eutrophication (FE) and human toxicity (HT) [252]. A LCA from cradle to cradle [247]

946 showed that BC production and application as adsorbent presented, compared to GAC

947 deriving from virgin non-renewable feedstock, lower environmental impacts in terms of

948 climate change (CC), fossil depletion (FD), freshwater eutrophication (FE) and terrestrial

949 acidification (TA) impact categories, and that wood and wood chips achieved the highest

950 environmental credits among the others feedstocks. In details, considering CC (expressed

951 as kg CO_2/kg adsorption material), GAC produced 1.44, while wood chips and corn stover

952 had credits ranging between -3.42 to -3.57, whereas oil palm produced 11.1 [253].

953 Regarding FE (evaluated as kg P eq/ kg adsorption material), BC from lignocellulosic

954 feedstock exhibited higher values than GAC, respectively ranging between 6.2 to 10.9 %

955 [247], due to the organic matter of renewable feedstock [254]. Considering both TA and

956 FD (respectively estimated as kg SO_2 eq/ kg adsorption material and kg oil eq/ kg

957 adsorption material), BC from lignocellulosic feedstock achieved higher credits than

958 GAC, between 9.5 % and 32.0 %.

959 Considering BC application in AD processes (perspective 3), to our knowledge the

960 available scientific literature only focused on sequential processes, as pyrolysis followed

961 by AD. A LCA from cradle to grave [255] considered BC produced from corn stover

962 applied as carburant and soil amendment with sequential AD, achieving respectively: -

963   2.47 kg CO$_2$eq/t and energy saving of -6.53 MJ/ t for the first scenario and - 4.67 kg

964   CO$_2$eq/t and energy saving of -9.73 MJ/ t for the second scenario.

965

966   Table 13. Environmental assessment of biochar (BC) production and uses

	Positive effects	Negative effects
Feedstock (perspective 1)	Lignocellulosic biomass exhibited more positive effects because of higher energy potential [247] Waste biomasses presented more advantages (e.g. avoided waste management) [256]	Feedstock provision (transport) [93] Potential presence of contaminants (heavy metals, persistent organic pollutants) in waste feedstocks (sewage sludge) [256]
Production process (perspective 2)	Renewable energy from syngas and bio-oil [93] Stabilization of C in biomass feedstock [18]	Large centralized pyrolysis units higher transportation distances compared to smaller decentralized units [256]
Activation process (perspective 2)		Activation was proven to represent a high item cost both in terms of economic and environmental perspectives [250]. Use of chemicals and electricity is associated to higher impacts [257].
Applications		
Soil improver	Biochar (C) sequestration in the soil [93] Reduced fertiliser requirements [93] Reduced N$_2$O emissions from soil [93] Enhanced plants growth [18] Reduced fossil fuel use in irrigation and cultivation [18] Enhanced nutrient availability [258] Increased H$_2$O retention [258] Reduced leaching and run-off of nutrients [258]	Binding /deactivation of pesticides, herbicides and nutrients in soil [258] BC as source of potential toxicants (heavy metals, PAHs, organics) [258]
Adsorbent	BC lower impacts than activated carbon [247]	

967
968

969   In conclusion, focusing the environmental assessment on perspective 4, the integration of

970   AD of waste biomass and pyrolysis of digestate, as shown in Figure 2, could increase the

67

971 net electricity production respect to AD alone [80] and enhance its quality as soil

972 amendment [81] with economic and environmental benefits [242]. In conclusion, the

973 integrated approach has been investigated by life cycle analysis and exhibited positive

974 environmental outcomes if compared with non-integrated processes [255,259].

975 **6. Conclusions**

976 This review addressed three key issues related to the comprehension of BC role in AD

977 processes:

978 *1. Investigation of the influence of BC properties on AD performances and of their ability*

979 *to counteract its main challenges*. It is understood that BC properties are determined

980 by the feedstock and by pyrolysis and activation processes. The key features were

981 SSA, porous structure and distribution, nature of surface functional groups (related to

982 CEC and adsorption capacity, buffer capacity, ability to immobilize microbial

983 communities), elemental composition and ash content. However, some mechanisms

984 (e.g. BC role in ammonium adsorption and BC influence on microbial mechanisms)

985 still need to be fully understood and explained. Other challenges for future research

986 are related to digestate management; in detail, the influence of BC relatively high doses

987 on the rheological properties of the digestate should be explored, as well as the

988 eventual leaching of pollutants in the environment as a consequence of digestate

989 recovery as soil improver.

990 *2. Assessment of the optimal BC production chain (i.e. feedstock-pyrolysis-activation) to*

991 *achieve the desired features*. Lignocellulosic biomasses, slow pyrolysis and physical

992 activation seemed to be a good combination in general, while other feedstocks and/or

993 chemical activation should be evaluated for specific needs and tailor-made applications.

However, a systematic investigation of the correlations linking BC physico-chemical characteristics and AD performances, carefully exploring one by one the BC effects mentioned in this review, is highly needed for a deep understanding of BC role as additive in AD processes.

3. Evaluation of the economic and environmental advantages connected to BC use in AD processes, compared to conventional solutions applied to address AD challenges. The main research gap related to this issue is the absence of specific literature related to BC use in AD processes, therefore only general statements could be formulated. The use of BC as additive could be cheaper and has less environmental impacts than of conventional AD improvers (e.g. physico-chemical-biological pre-treatments) and of GAC. The integration of AD and pyrolysis achieved economic feasibility and positive environmental performances if compared with non-integrated processes. Future research could investigate the optimization of technical, economic and environmental performances of BC production chain and its integration in AD processes.

Acknowledgements

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